University of Alberta

Reduction of Mechanical Entrainment of Fine Hydrophilic Particles Through the Use of Polymeric Depressants during Froth Flotation

by

David Wannas ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the
requirements for the degree of Master of Science

In

Materials Engineering

Department of Chemical and Materials Engineering

Edmonton, Alberta

Fall, 2005

Library and
Archives Canada

Published Heritage
Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et
Archives Canada

Direction du
Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence
ISBN: 0-494-09310-2
Our file Notre référence
ISBN: 0-494-09310-2

NOTICE:
The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:
L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Canada

ABSTRACT

Fine particles pose two challenging problems in the froth flotation process. The first problem is the difficulty in effectively floating and recovering hydrophobic particles, mainly due to their small mass and high surface area. The second problem involves the high mechanical entrainment of fine hydrophilic particles due to their small size. Much research has been conducted to improve the flotation rate of fine hydrophobic particles, while the hydrophilic particles are kept highly dispersed in these systems. As a result not only does the problem of mechanical entrainment still remain, but it is also further aggravated by the techniques developed by such research. The resulting consequence of such techniques is an improved recovery but lower grade of the hydrophobic particles; the lower grade being attributed to the entrainment of the hydrophilic (gangue) particles.

The objective of this thesis was to verify the positive correlation between particle size of hydrophilic particles and mechanical entrainment, and to use polymeric depressants to flocculate and thus increase the particle sizes of these hydrophilic particles so that their entrainment and recovery into the froth would be minimized. Using a number of various dispersants and polymeric depressants, tests were performed to minimize the mechanical entrainment of hematite and hydroxylapatite, each separately, in the flotation of quartz. Sodium silicate dispersant in conjunction with corn starch depressant appeared to be the most effective in minimizing the entrainment of these minerals, particularly hematite.

ACKNOWLEDGMENTS

I would like to thank my supervisor, Dr. Qi Liu for his unwavering help, support and patience throughout this research project.

I would also like to thank NSERC for providing all the necessary funding for this project.

Last but not least I would like to extend my thanks to Zhangming Cui for assisting me in getting started with my tests, and showing me my way around the laboratory, Jim Skwarok for showing me how to operate the Malvern 2000 particle size analyzer, and my fellow students, Mingli Cao, Weibing Gan, and Amir Babak Yazdani for their moral support and encouragement.

TABLE OF CONTENTS

1 INTRODUCTION....................1
2 LITERATURE SURVEY....................3
  2.1 Problems Associated With Fine Particle Flotation....................3
  2.2 Characteristics of Fines and Ultrafines on the Flotation Process....................4
    2.2.1 Slow Rate of Flotation....................5
    2.2.2 Reagent Consumption....................5
    2.2.3 Froth Characteristics....................6
    2.2.4 Surface Coating....................6
    2.2.5 Mechanical Entrainment....................7
  2.3 Conditions Influencing the Flotation of Fine Particles....................8
    2.3.1 The Effect of Bubble Size on the Flotation of Fine Particles....................8
    2.3.2 The Effect of Particle Charge on the Flotation of Fine Particles....................9
  2.4 Previous Studies for Improving Fine Particle Flotation....................10
    2.4.1 Techniques Based on Process Design....................11
      2.4.1.1 Hydrophobic Flocculation and Floc Flotation....................11
      2.4.1.2 The Use of Ultrasound in Fine Particle Flotation....................16
      2.4.1.3 Carrier Flotation....................18
      2.4.1.4 Dissolved Air Flotation (DAF)....................19
      2.4.1.5 High Temperature Conditioning....................20
      2.4.1.6 Split Conditioning and Combined Flotation (SCCF)....................21
    2.4.2 Techniques Based on Equipment Design....................21
      2.4.2.1 Column Flotation....................21
      2.4.2.2 Leeds Column Cell....................22
      2.4.2.3 Packed Column Cell....................22
      2.4.2.4 Jameson Cell....................23
      2.4.2.5 Hybrid Cells....................24
      2.4.2.6 Air Sparged Hydrocyclone Flotation (ASH)....................25
      2.4.2.7 Rapid Flotation System....................25
    2.4.3 Techniques Based on Reagent Design....................26

2.4.3.1 Chemisorbing Flotation Collectors....26
2.4.3.2 Addition of Collector Before Grinding....26
2.4.3.3 Extender Flotation....27
2.4.4 Methods for Examining and Reducing Entrainment during Flotation....28
2.5 Commentary on Previous Work Done....31
2.6 General Theory of Particle Interactions....32
2.6.1 Particle Coagulation....32
2.6.2 Particle Flocculation....33
2.6.3 Dispersion....34
2.7 Flocculation Characteristics of Various Minerals....34
2.7.1 Hematite and Hydroxylapatite....34
2.7.2 Quartz....37
3 OBJECTIVE....38
4 EXPERIMENTAL....39
4.1 Minerals Used....39
4.2 Reagents....39
4.3 Reagent preparation....41
4.3.1 Corn Starch and Dextrin Stock Solutions....41
4.3.2 Carboxymethyl cellulose (CMC, M.W= 80,000 and 700,000) Stock Solutions....42
4.3.3 Dispersant Preparations....42
4.3.4 Collector Preparation....42
4.4 Settling tests procedures....43
4.5 Single Mineral Flotation Test Procedures....44
4.6 Two Mineral Flotation Test Procedures....46
4.7 Agitation Procedures....48
4.8 Particle Size Analysis Procedures....50
4.9 Zeta Potential Analysis Procedures....51
5 RESULTS AND DISCUSSION....53
5.1 Single Mineral Settling and Flotation Behavior....53
5.1.1 Hematite (Fe_2O_3)....53

5.1.2 Hydroxylapatite ($Ca_5(OH)(PO_4)_3$)....55
5.1.3 Sphalerite (ZnS)....56
5.1.4 Galena (PbS)....57
5.2 Two Mineral Flotation Behavior....66
5.2.1 Hematite/Coarse Quartz Flotation....66
5.2.2 Hematite/Fine Quartz Flotation....69
5.2.2.1 Hydrophobic Flocculation (Agitation Tests)....69
5.2.2.2 Settling Behavior of Hematite/Fine Quartz....73
5.2.2.3 Flotation Behavior of Hematite/Fine Quartz....74
5.2.3 Hydroxylapatite/Coarse Quartz Flotation....77
5.2.4 Hydroxylapatite/Fine Quartz Flotation....80
5.2.4.1 Hydrophobic Flocculation....80
5.2.4.2 Flotation Behavior of Hydroxylapatite/Fine Quartz....81
5.2.4.3 Hydroxylapatite and Fine Quartz Flotation Behavior as a Function of pH....82
5.3 Mechanistic Aspect of the Reduction of Entrainment....101
5.3.1 Particle Size Analysis....101
5.3.2 Zeta Potential Analysis....103
6 CONCLUSIONS....117
7 RECOMMENDATIONS FOR FURTHER RESEARCH....122
8 REFERENCES....124

List of Tables

Table 1 Particle Size Classification (Sivamohan and Forssberg, 1985)......................3

Table 2 Minerals used in Research..39

Table 3 Reagents used in Research..40

Table 4 Separation Efficiencies of the Cationic Collector Flotation of Coarse Quartz-Iron Oxide Mixtures at pH 10 with Various Reagents.......................66

Table 5 Separation Efficiencies of Cationic Collector Flotation of Fine Quartz-Iron Oxide Mixtures at pH 10 with Various Reagents......................75

Table 6 Separation Efficiencies of Cationic Collector Flotation of Coarse Quartz- Hydroxylapatite Mixtures at pH 10 with Various Reagents...............78

Table 7 Separation Efficiencies of Cationic Collector Flotation of Fine Quartz- Hydroxylapatite Mixtures at pH 10 with Various Reagents...............81

Table 8 Effect of Various Reagents and Conditions on the Particle Size of Hematite...102

Table 9 Effect of Various Reagents and Conditions on the Particle Size of Hydroxylapatite...103

List of Figures

Figure 1 Schematic Diagram Illustrating the Relationship Between the Physical and Chemical Properties of Fine Particles and their Behavior in Flotation. (Subrahmanyam and Forssberg,1988)........4

Figure 2 Schematic Representation of Hydrophobic Flocculation of Fine Particles (Song et al., 1999)........12

Figure 3 The Jameson Cell (Xstrata Technology, 2004)........23

Figure 4 Schematic Illustration of the Rushton Impeller and a Vertical Cross-Sectional View of the Agitation Cell used in the Agitation Procedures........49

Figure 5 Hematite Flocculation and Settling Behavior........59

Figure 6 Entrainment Behavior of Hematite........60

Figure 7 Hydroxylapatite Flocculation and Settling Behavior........61

Figure 8 Entrainment Behavior of Hydroxylapatite........62

Figure 9 Sphalerite Flocculation and Settling Behavior........63

Figure 10 Entrainment Behavior of Sphalerite........64

Figure 11 Entrainment Behavior of Galena........65

Figure 12 Hematite/Coarse Quartz Flotation Behavior........84

Figure 13 Alternative Representation for Hematite/Coarse Quartz Flotation Behavior........85

Figure 14 Quartz Recovery as a Function of Agitation Speed at 5 Minutes........86

Figure 15 Quartz Recovery as a Function of Agitation Speed at 15 Minutes........87

Figure 16 Quartz Recovery as a Function of Agitation Speed at 20 minutes........88

Figure 17 Influence of DDA Collector on the Flocculation of Quartz........89

Figure 18 Quartz Flocculation Behavior as a Function of DDA Concentration........90

Figure 19 Hematite Recovery as a Function of Agitation Speed at 5 Minutes........91

Figure 20 Hematite/Fine Quartz Flocculation Behavior........92

Figure 21 Hematite/Fine Quartz Flotation Behavior........93

Figure 22 Hydroxylapatite/Coarse Quartz Flotation Behavior.....94
Figure 23 Hydroxylapatite/Fine Quartz Recovery as a Function of Agitation Speed at 15 Minutes.....95
Figure 24 Hydroxylapatite/Fine Quartz Flotation Behavior.....96
Figure 25 Quartz Recovery as a Function of pH at a DDA Concentration of 10^{-5} mol/L.....97
Figure 26 Quartz Recovery as a Function of pH at a DDA Concentration of 10^{-4} mol/L.....98
Figure 27 Hydroxylapatite Recovery as a Function of pH at a DDA Concentration of 10^{-4} mol/L.....99
Figure 28 Hydroxylapatite/Quartz Recovery as a Function of pH at a DDA Concentration of 10^{-4} mol/L.....100
Figure 29 Effect of Various Reagents on the Zeta Potential for Hematite.....109
Figure 30 Effect of Various Reagents on the Zeta Potential for Hydroxylapatite.....110
Figure 31 Effect of Various Reagents on the Zeta Potential for Fine Quartz.....111
Figure 32 Effect of pH on the Zeta Potential of Starch in the Presence and Absence DDA.....112
Figure 33 Effect of 50 ppm Corn Starch on the Zeta Potential for Fine Quartz, Hydroxylapatite, and Hematite.....113
Figure 34 Effect of 50 ppm Sodium Metaphosphate on the Zeta Potential for Fine Quartz, Hydroxylapatite, and Hematite.....114
Figure 35 Effect of 10^{-4} mol/L of DDA Collector on theZeta Potential for Fine Quartz, Hydroxylapatite, and Hematite.....115
Figure 36 Effect of no Reagent on the Zeta Potential for Fine Quartz, Hydroxylapatite, and Hematite.....116

1 INTRODUCTION

The froth flotation process is the most important and widely used mineral processing technique in the minerals industry. Originally patented in 1906, the flotation process has allowed for the mining of low-grade and complex ore bodies that were previously considered as uneconomic. Due to its selectivity, the process can be effectively used to achieve specific separations from complex ores such as lead-zinc, copper-lead, etc. Although flotation was initially developed to treat the sulphides of copper, lead, and zinc, the flotation process has grown such that it is now widely used to treat oxides, such as hematite and cassiterite, oxidized minerals, such as malachite and cerussite, and non-metallic ores, such as fluorite, phosphates, and fine coal, etc. (Wills, 1997).

The froth flotation process is based on the difference in the physical and chemical surface properties of the particles of the various minerals. The property differences of the minerals within the pulp become apparent once they are treated with specific reagents. However, in order for separation to occur, air bubbles must attach themselves to a particle which is carried up over to the water surface. Such a procedure can only be applied to fairly fine particles since if the particles are too large, the adhesion between the particle and the bubble will be less than the particle weight causing the bubble to drop its load. During flotation concentration, the mineral is usually transferred to the froth, leaving behind the gangue in the pulp, also known as the tailing. Such a procedure is known as direct flotation. In some instances however, the gangue is separated into the float fraction instead, and the valuable mineral remains in the pulp (reverse flotation). Flotation reagents are of vital importance to the froth flotation process and it is also crucial that they possess selectivity such that they are capable of rendering the mineral of interest hydrophobic.

Although the flotation process is widely used in mineral processing industries, certain limitations exist. Perhaps the largest limitation is associated with the separation of very fine or ultrafine particles. In order to properly liberate valuable minerals in a finely-disseminated ore, very fine grinding of the ore is required. This fine grinding results in fine particles that are then carried over onto various separation processes such as froth flotation. The problem with these very small particles is that the hydrophobic particles are not floated effectively due to low particle inertia which causes infrequent bubble-particle collision, while the hydrophilic particles tend to be carried to the froth layer by mechanical entrainment. Both extremes can and do impose problems for many industries. For example if during a flotation process, an industry is interested in recovering particles of a certain fine mineral, the lack of floatability of that mineral due to its fineness can lead to a low recovery of that mineral. Alternatively, assume that the same industry was capable of recovering the mineral yet the gangue hydrophilic mineral was mechanically entrained due to its fine size thus interfering with the separation process. The result in this case is a low grade of the mineral product. Such problems continue to be faced by mineral processing industries all over the world. Many methods have been used over the years to ensure that high grade concentrates would result with a high recovery. However many of these techniques have been developed with the objective of improving the recovery of the hydrophobic particles, while the problems associated with entrainment of hydrophilic particles have been almost completely ignored.

This thesis discusses in detail the problems associated with fine particle flotation. This discussion is followed by an experimental study to minimize mechanical entrainment of fine gangue particles in the flotation process.

2 LITERATURE SURVEY

2.1 Problems Associated With Fine Particle Flotation

Fine and ultrafine particles impose a problem in the froth flotation process. According to Singh et al. (1997), the fine particles are slow to float and it is widely accepted that the low flotation rate is mainly the result of the reduced collision efficiency of the fine particles with air bubbles. In addition to this, fine particles interfere with the flotation of intermediate and coarse sized particles due to their high surface area which consumes a disproportionate amount of flotation reagents. The presence of fine particles in the flotation process also affects the overall efficiency of the flotation process (flotation rate, recovery and grade) by (i) influencing the froth characteristics, (ii) undesirable activation due to dissociation of the ions from the surface of fine particles, (iii) non-selective adsorption of the reagents, (iv) the tendency to form a surface coating (Singh et al. 1997). The effects of particle size on the flotation of minerals was first carried out by Gaudin et al. (1931) who discovered that the highest recoveries for lead and zinc sulphides were in the particle size range of 10-50 microns. Many researchers including Trahar and Warren (1976) reviewed the floatability of fine particles. Although many sources have various definitions of particle size classification, Trahar (1981) presented an arbitrary classification of particles on the basis of their floatabilities as follows: fine particles (5-10 μm), intermediate (10-70 μm), and coarse particles (> 70 μm). Sivamohan and Forssberg (1985) have proposed a different classification of particle sizes presented in Table 1.

Table 1 Particle Size Classification (Sivamohan and Forssberg, 1985)

Super colloids	Particles < 0.2 microns
Colloids	Particles < 1 microns
Ultrafines	Particles < 5 microns
Very fines	Particles < 20 microns
Fines	Particles < 100 microns
Intermediates	Particles < 500 microns
Coarse	Particles > 500 microns

Studies by various researchers have shown that in general flotation recovery is best in the size range of 10-100 microns although the optimum size depends on the specific mineral. In addition to this studies have shown that flotation rate decreases with a decrease in particle size and the grade of the concentrate also decreases with the decrease in particle size (Trahar, 1976).

2.2 Characteristics of Fines and Ultrafines In the Flotation Process

Figure 1 summarizes the relationship between the physical and chemical properties of fine particles and their behavior in flotation.

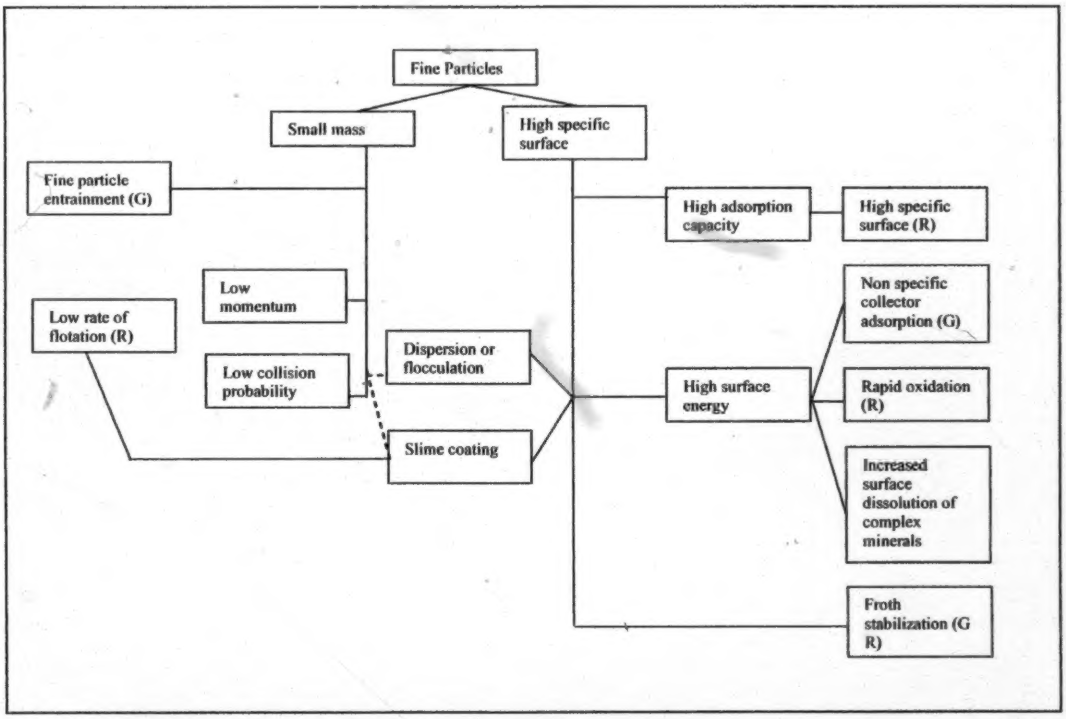

Fine Particles
Small mass
High specific surface
Fine particle entrainment (G)
High adsorption capacity
High specific surface (R)
Low momentum
Non specific collector adsorption (G)
Low rate of flotation (R)
Dispersion or flocculation
Low collision probability
High surface energy
Rapid oxidation (R)
Slime coating
Increased surface dissolution of complex minerals
Froth stabilization (G R)

Figure 1: Schematic Diagram Illustrating the Relationship Between the Physical and Chemical Properties of Fine Particles and their Behavior in Flotation. (G) and (R) Refer to Whether the Phenomenon Affects Grade and/Recovery (Subrahmanyam and Forssberg, 1988)

2.2.1 Slow Rate of Flotation

In the same mineral range of 1-30 μm, the rate at which ultrafine particles are recovered by froth flotation is less than that of larger particles (Warren, 1984). Many researchers have agreed that the reason for such behavior is the low collision rate between the fine particles and the bubbles. One formula that was developed for analyzing the relationship between particle size and flotation rate is $k \propto d^n$, where k is a suitable measure of the flotation rate, d is the particle diameter, and n is a number between 1.5 and 2 (Trahar, 1981). Various trends have been observed whereby bubble sizes in the flotation process were modified so that the probability of collision of fine particles with bubbles was greatly increased. These trends will be discussed in later sections.

2.2.2 Reagent Consumption

As can be seen from Figure 1, fine particles possess a high specific surface area, thus a high adsorption capacity and a high surface energy. The main problem associated with such a high specific surface area is the non selective adsorption of reagents. Flotation collectors, modifiers, and possibly some frothers are adsorbed by fine mineral particles, the extent being dependent on the reagent concentration in the flotation pulp. The postulated increase in surface energy per unit surface area with decrease in size is believed to be a result of an increased proportion of edges and corners (Welch, 1952) and of cracks, dislocations and other lattice defects (Leja, 1952) arising from size reduction operations. Clearly such characteristics would suggest that fine particles interfere with the selectivity of various reagents required in the flotation process. The result can be devastating since more reagents would be consumed and the desired outcome intended by these reagents may not be fully achieved. Trahar (1981) has discussed the flotation characteristics of coarse particles in the presence of fine particles in that the presumed rapid and disproportionate consumption of collector by fine particles leads to less complete surface coverage of the coarse particles which are accordingly less floatable. However, Trahar (1981) argued that such a statement is true only in the sense that when the proportion of fines is large so that the adsorption density of the reagent on all particles is reduced, a poor recovery of the coarse particles results.

2.2.3 Froth Characteristics

In general, fine and ultrafine particles tend to stabilize the froth. A stable froth is desirable; however too stable a froth is often difficult to handle (Subrahmanyam and Forssberg, 1988), and at the same time may cause water recovery to be too high leading to a high recovery of entrained gangue particles (Ross, 1990).

2.2.4 Surface Coating

Many laboratory studies have indicated that fine and ultrafine particles have a tendency to form slime coatings on coarse particles. Taggart (1927) claimed that the control of slime coatings was the most important factor in differential flotation. Many other researchers considered Taggart's claim to be somewhat of an overstatement. Based on laboratory tests conducted, slime coatings have been found to cover less than half the surface of coarse particles. The slime coating by fine particles has been found to interfere with the flotation process. Warren (1981) claimed that according to work performed by Fuerstenau et al. (1958), 25 percent coverage of quartz with iron oxide slime prevented the Hallimond-tube-flotation of the quartz with amine. In addition to this, the possibility of a chemical reaction between the slime coatings and the coarse particles after contact does exist (Warren, 1981) and should not be ignored since the grade of the concentrate can be affected. Work performed by various researchers have led to conclusions that particle and substrate charge played a role in determining whether or not slime coating would occur. The effect of particle charge on fine particle flotation will be explored in a later section. As mentioned earlier slime coatings by ultrafine and fine particles were studied in laboratory model systems. In practice the problem has not been reported on larger flotation machines or in operating plants. According to Warren (1981), if slime coating does occur on larger scale flotation systems, it must do so in a turbulent environment where the collision rate between fine and coarse particles is affected by the fluid flow regime and hydrodynamic interactions. Slime coatings have been used to advantage in a process known as carrier flotation, which will be described later.

2.2.5 Mechanical Entrainment

The two most important mechanisms by which particle collection takes place in a flotation operation are adhesion and entrainment (Subrahmanyam and Forssberg, 1988). Entrapment and carrier flotation are two other mechanisms. According to Smith and Warren (1989), in a conventional flotation cell hydrophilic gangue particles are recovered into the concentrate by at least three possible methods, namely: (i) recovery via aggregates attached to air bubbles by hydrophobic particles in the aggregate, such as in slime coatings, (ii) recovery through composite particles attached to air bubbles by their hydrophobic portion, and (iii) mechanical entrainment in the inter-bubble water. Although not much attention has been given to the problem of mechanical entrainment of fine gangue particles during froth flotation, mechanical entrainment is no doubt a major problem in the flotation of fine particles since the grade of the concentrate is lowered when fine gangue hydrophilic particles enter the froth alongside the valuable hydrophobic particles. For particles < 10 μm the collision efficiencies are low and the mechanism of collection takes place by entrainment. It is important to note that mechanical entrainment of fine gangue particles was well recognized for a long time. Due to their light weight, fine particles have a higher tendency to be easily entrained compared to coarser ones. Such a statement clearly identifies mechanical entrainment as the main source for the recovery of fine gangue to the froth. In fact entrainment is a characteristic feature of fine particles and is non-selective, with no distinction between hydrophilic or hydrophobic particles. Entrainment occurs when fine or ultrafine gangue particles enter the base of the froth column suspended in the water occupying the spaces between the bubbles as opposed to being attached to the bubbles. These particles are subsequently carried over into the concentrate via the water remaining in the topmost layers of the froth. For hydrophobic particles, the recovery by entrainment is measured by differences in the relative contributions of true flotation in the presence of collector and by entrainment in the absence of the collector, i.e., with frother only present at the same water recoveries (Trahar, 1981). Although drainage of gangue particles is possible, the finer the gangue particles, the less likely they are to drain back into the pulp. Mechanical entrainment of fine particles is directly proportional to the water recovered into the froth. In other words, the higher the percentage of water recovered, the higher is the percentage of entrained gangue recovered into the concentrate. This is a direct result of the particles remaining suspended in the inter-bubble water. The relationship between the recovery of fine gangue by entrainment and the recovery of water is represented by the equation: $R_g = e_g R_{water}$ (Subrahmanyam and Forssberg, 1988), where R_g is the recovery of fine gangue of a given size in a given time, e_g is a constant for a given particle size and specific gravity and R_{water} is the recovery of water for the same time period. The slope of the line e_g in the plot of the recovery of solids versus the recovery of water is defined as the degree of entrainment. This is the same concept defined by Trahar (1981). At this point it is important to note that a clear distinction should be made between entrainment and "entrapment" whereby in entrapment, non-floatable particles are held in the froth by bridging across floatable particles held by adjoining bubbles. In most cases however, entrapment is not significant under the turbulent commercial conditions.

2.3 Conditions Influencing the Flotation of Fine Particles

Although it has already been established that there are a number of problems associated with fine particle flotation, there are certain conditions that play a role in influencing the degree to which the problems of fine particle flotation dominate the froth flotation process. In addition to solution pH, the two other major conditions influencing the flotation of fine particles are bubble size and particle charge.

2.3.1 The Effect of Bubble Size on the Flotation of Fine Particles

In the flotation process, bubbles play an important role of actually separating the valuable minerals from the liquid phase and gangue which ultimately leads to their removal. It is clear that the size of the bubbles involved would be intimately linked to the removal process. In fact, bubble size is one of the crucial physical variables determining the flotation efficiency. As mentioned earlier it is the bubble-particle collisions that are necessary for the attachment and subsequent removal of the solids. Reay and Ratcliff (1975) defined collection efficiency of bubbles as $E \propto d_b^{-1.9}$, where d_b is the bubble diameter. Such a formula suggests that the larger the bubble diameter, the lower the collection efficiency. Most of the reported experiments involving the effect of bubble size on the flotation of fine particles were performed under highly idealized conditions i.e., in quiescent systems with the bubbles rising at their terminal velocity, which in reality are far from the conditions faced by practical flotation cells.

Ahmed and Jameson (1985) carried out a number of flotation tests with fine particles of polystyrene latex, quartz, and zircon, to determine the role of bubble size on the flotation of fine particles. Their main findings were that the rate of flotation of fines was accelerated considerably by using very small bubbles, primarily less than 100 μm in diameter. The results strongly support the idea that serious consideration should be given to creating separate flotation circuits for specifically handling the fine size ranges as argued by Trahar (1981). Such findings may well indicate that fine bubbles may also play a role in increasing the entrainment of fine hydrophilic particles.

2.3.2 *The Effect of Particle Charge on the Flotation of Fine Particles*

Particle charge plays an important role in the flotation process and can be used to effectively influence the flotation of fine particles. Derjaguin and Shukakidse (1993) examined the effect of particle charge on flotation by measuring the zeta potential of naturally hydrophobic antimonite particles. They determined that the rate of flotation dropped drastically as the zeta potential of the particles was increased beyond a critical value. They also studied this phenomenon by analyzing the adsorption of a cationic surfactant onto negatively charged silver iodide particles, and found that the flotation rate measured in a Hallimond tube was highest when the zeta potential of the silver iodide was zero. This behavior was also observed by Vivo and Karger (1970) for clay particles.

In both cases however, it is possible that coagulation may have occurred as a result of the zeta potential being zero and thus this increase in particle size may have caused the increase in the flotation rate (Derjaguin and Shukakidse, 1993). In the earlier work of Collins and Jameson (1976), experiments were performed whereby the effects of particle size and charge on the rate of flotation of fine polystyrene particles (4-20 μm) were measured. The polystyrene particles were floated in the presence of cetyl trimethylammonium bromide (CTAB) as collector/frother and the charge was controlled by the addition of sodium sulfate. It was observed that the flotation rate constant k, varied by the relationship $k \propto d_p^{1.5}$; the exponent, however, showed little dependence on the charge of the particle which was varied in the range of 30-60 mV. The particle charge however, appeared to have a very significant effect on the flotation rate constant which was altered by almost an order of magnitude when the mobility was altered from 2.7 to 5.2 μm/s/V/cm. Therefore, it is believed that the maximum rate of flotation is achieved when the zeta potential of particles is zero. As the charge of the particles and the bubbles build up, coalescence between them is inhibited by double-layer potential.

2.4 Previous Studies for Improving Fine Particle Flotation

This section discusses technologies developed to improve the flotation of fine particles. The key to the success of many of these processes is the selectivity of the reagents to specific minerals. In some of these technologies, examples of work done by researchers using the various methods will be discussed along with their findings.

2.4.1 Techniques Based on Process Design

2.4.1.1 Hydrophobic Flocculation and Floc Flotation

Perhaps one of the most widely tested methods by mineral processing industries for improving the flotation of fine particles is hydrophobic flocculation of fine particles (usually the fine valuable minerals) followed by the flotation of these newly formed flocs (floc flotation). The hydrophobic flocculation process can be divided into two steps: the formation of hydrophobic flocs, and the separation of these newly formed flocs from other matter present in the flotation pulp.

The key to the success of hydrophobic flocculation is that the particles of a specific mineral form hydrophobic flocs while all of the other minerals remain in dispersion (Song et al., 1999). In order to carry out this process, three procedures are required, namely: dispersion, selective hydrophobization, and hydrophobic flocculation. Dispersion is crucial in that it helps stabilize fine mineral particles to prevent hetero-coagulation (two or more fine minerals adhering to each other) from occurring, which would defeat the purpose of the separation process. Dispersants are usually added in either grinding mills during size reduction or in mixing tanks. Examples of typical dispersants used include sodium silicate, tannic acid, and sodium hexametaphosphate. Selective hydrophobization is used for minerals that are not hydrophobic in nature. Basically selective hydrophobization is accomplished by adding special collectors which selectively render particular mineral particles hydrophobic upon their adsorption. The final procedure, hydrophobic flocculation is usually achieved in a mechanical mixing tank whereby kinetic energy is provided mechanically to hydrophobic particles causing them to collide with each other and surmount the energy barrier between them due to electric double layer repulsion and water films (Song et al., 1999). The result is the formation of hydrophobic flocs, produced as a result of hydrophobic interaction between the particles and the kinetic energy input. Figure 2 represents a schematic of the hydrophobic flocculation of fine particles in an aqueous suspension. The block arrows represent the three stages involved in hydrophobic flocculation as described above

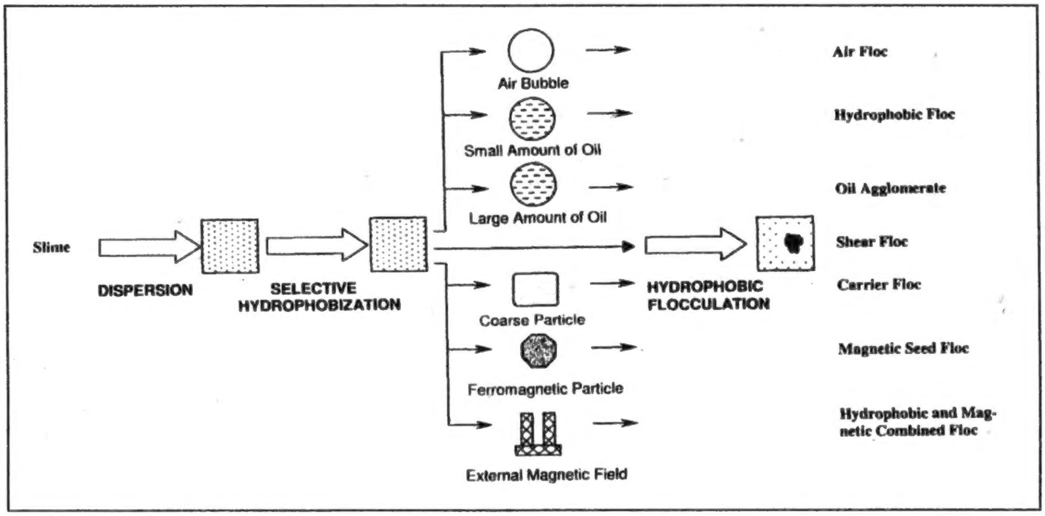

Slime
DISPERSION
SELECTIVE HYDROPHOBIZATION
Air Bubble
Small Amount of Oil
Large Amount of Oil
Coarse Particle
Ferromagnetic Particle
External Magnetic Field
HYDROPHOBIC FLOCCULATION
Air Floc
Hydrophobic Floc
Oil Agglomerate
Shear Floc
Carrier Floc
Magnetic Seed Floc
Hydrophobic and Magnetic Combined Floc

Figure 2: Schematic Representation of Hydrophobic Flocculation of Fine Particles (Song et al., 1999)

By carefully observing Figure 2, it can be seen that the hydrophobic flocs may have various sizes, structures and properties depending on the special matters and forces involved in the stages of hydrophobic flocculation. Shear flocculation occurs in hydrophobic particles which have been provided kinetic energy mechanically. However, some researchers consider that shear flocculation may not be appropriate for fine mineral processing due to the small flocs and the requirement for high energy consumption (Subrahmanyam and Forssberg, 1990). Hydrophobic flocculation is greatly improved with the addition of a small amount of non-polar oil. The addition of this non-polar oil causes flocs to become more compact and increases the degree of aggregation. It is important to note that this enhancement by the addition of non-polar oil does not cause a decrease in selectivity. It was defined that hydrophobic flocculation involved the phenomenon whereby hydrophobic particles aggregate due to sufficient kinetic energy and non-polar oil addition. Shear flocculation is considered a special case of hydrophobic flocculation.

If their pores are filled up with non-polar oil, hydrophobic flocs appear as pellets. In this case the phenomenon is called oil agglomeration. In order for oil agglomeration to work, large amounts of non-polar oil need to be added. Oil agglomerates are usually very big in size and behave as real solid particles (Cebeci, 2003). The introduction of micro-bubbles to the hydrophobic flocculation process could greatly enhance the aggregation by forming air flocs of hydrophobic particles. This enhancement is due to the fact that air bubbles are strongly hydrophobic. Hydrophobic flocculation can be enhanced for paramagnetic particles by conditioning the suspension in an external magnetic field (Song et al., 1999).

Separation methods of hydrophobic flocs from dispersed particles are usually chosen according to the properties of the flocs, including size, density, and magnetic properties. These methods include: flotation, magnetic separation, sedimentation, and screening. Flotation is not only the most important and common method of separation, but in addition it is also the method of interest in this research. Unless the flocs are too large, flotation is the common way for recovering hydrophobic flocs due to their hydrophobic surfaces. Experimental results (Song and Lu, 1989) indicated that hydrophobic flocs behave in a similar fashion as real solid particles with the same size range in froth flotation. Therefore flotation cells and columns can apply to hydrophobic flocs without any modification. This process of flotation after hydrophobic flocculation is referred to as floc flotation. In floc flotation, it is the flocs instead of individual fine particles that interact with air bubbles, thus avoiding the problem of low probability of collision and adhesion of mineral fines to air bubbles. This is the idea behind floc-flotation in that the aggregates of fine particles behave in a manner as if they were single larger particles, therefore attaching more easily to bubbles and exhibiting an increased rate of flotation. There are at least four possible mechanisms responsible for the flocs being lifted to the top of the pulp and onto the froth layer, these include: attachment of the gas bubbles to the floc, physical entrapment of rising bubbles under the floc, co-flocculation of bubbles and particles as the floc is developed, and nucleation and growth of bubbles inside flocs after the pressure is released (Warren, 1984).

Magnetic separation is good for hydrophobic flocs with a high magnetic susceptibility. Screening is best used for big and compact flocs such as oil agglomerates. Finally, sedimentation can be applied to all kinds of hydrophobic flocs except air flocs. The separation efficiency is comparatively quite low and is, therefore, recommended for cases where the density difference between valuable minerals and gangue is large. (Song et al., 1999).

There are many factors that influence the hydrophobic flocculation process. These include suspension stirring, particle surface charge, temperature, air bubble involvement, particle hydrophobicity, non-polar oil addition, and original particle size. Of these, the three main important factors are particle hydrophobicity, non-polar oil addition, and suspension stirring (Song et al., 1999). These three parameters will now be examined more closely.

Particle Hydrophobicity

The most important parameter influencing hydrophobic flocculation is particle hydrophobicity (Song et al., 1999). Experimental work was performed on rhodochrosite fines to examine this parameter. The rhodochrosite hydrophobicity, expressed in terms of contact angle, was adjusted through immersing the fines in sodium oleate solution at various concentrations. It was observed that no aggregation occurred to the fine particles with zero contact angle even though high shear field was applied to the suspension, leading the authors to believe that it was impossible to form flocs out of hydrophilic particles. However, the fine particles were strongly aggregated by means of suspension stirring in the presence of sodium oleate, which rendered the particles hydrophobic. Thus the conclusion from this work was that the more hydrophobic the particles, the more powerful the hydrophobic flocculation process.

Hydrophobic interaction is an unusually strong attraction between hydrophobic particles in aqueous solution, which arises from the rearrangements of hydrogen bond configurations in the overlapping solvation zones as two hydrophobic species come together (Song et al., 1999). Since hydrophobic attraction closely depends on particle hydrophobicity, it can be expected that hydrophobic flocculation is dominated by the hydrophobicity of the particles to be aggregated.

Non-Polar Oil Addition

Non-polar oils such as kerosene, diesel, and other fuel oils were found to greatly enhance hydrophobic flocculation. The mechanism of this effect is described in terms of an increase in both particle hydrophobicity and oil bridging. (1) Non-polar oil droplets in aqueous suspension spread on hydrophobic particle surfaces due to strong hydrophobic attraction between them, producing oil coverage on the particles and thus increasing their hydrophobicity. (2) When oil is involved in hydrophobic flocs, bridging of the hydrophobic particles occur. Due to this oil bridging mechanism, hydrophobic flocs become much stronger to sustain floc-rupture forces from turbulence, leading to a much more powerful flocculation (Song, et al, 1999). Many experiments have been carried out examining the addition of non-polar oil and its effects on hydrophobic flocculation. The conclusion drawn from the results was that the flocculation degree was much higher in the presence of non-polar oils such as kerosene than in the absence of these oils.

Suspension Stirring

Suspension stirring of a sufficient magnitude is crucial to provide hydrophobic particles with kinetic energy for generating good hydrophobic flocculation. Experimental evidence suggests that as the stirring speed is increased, the floc size drastically increases until a peak is reached, and then there is a sharp decline. The reason for the decline of the floc size in the range of high stirring speeds is due to strong floc-rupture forces that are greater than the floc strength.

Many experiments have been performed using hydrophobic flocculation followed by floc flotation, and the results overall proved that the procedure is very effective in improving fine particle flotation. For example, work has been done in examining the floc flotation of galena and sphalerite fines after hydrophobic flocculation (Song et al., 2001). The conclusions drawn from the results were that (i) Floc flotation response of galena and sphalerite fines was substantially increased when the fines were present in the form of flocs, generated by hydrophobic flocculation induced by potassium amyl xanthate and kinetic energy input. (ii) Floc flotation was dependent on the size of the flocs, and reached completion at an appropriate size, (iii) Floc flotation was improved considerably by the addition of a small amount of kerosene, which might have been attributed to not only the enhancement of the hydrophobic flocculation, but also the increase of adhesion probability of the flocs to air bubbles. (iv) Applying floc flotation to the fines not only reduced the losses of the valuable metals in the tailing through recovering more valuable mineral fines, but also considerably increased the separation efficiency in the cleaner flotation through increasing the flotation rate of valuable minerals, implying that flotation is indeed an effective potential means to beneficiate mineral fines.

2.4.1.2 The Use of Ultrasound in Fine Particle Flotation

Much work has been done in recent years to use ultrasound in the fine particle flotation process. It has been found that by using ultrasound in flotation, the separation efficiency of the process was greatly improved. A particularly important advantage of the use of ultrasound in flotation is its dispersing action which helps break down agglomerates, removes slime coatings from the surface of solids, and promotes emulsification (Letmathe et al., 2002).

The use of ultrasound in the flotation process has been used for a number of years now. According to Letmathe et al. (2002), in the 1930's, researchers such as Peterson (1951) have shown that with the use of ultrasound in flotation, water-insoluble flotation reagents form emulsions, which compared to those produced by means of mechanical agitation, enable a much higher solids recovery. In addition to this finding, cases of improved fine coal beneficiation by prior irradiation of the flotation pulp with ultrasound have been reported. Many other researchers have found that both the grade and recovery of the concentrate resulting from the froth flotation process was improved when using ultrasound.

Letmathe et al. (2002) have discussed the use of ultrasound in the various stages of the flotation process for fine graphite. The study was conducted using ultrasound separately in each stage, namely: the emulsification of the reagents, dispersion of the solids, and conditioning of the suspension. The use of ultrasound for each stage and the effect it had on flotation were then examined. The experimental studies on flotation with ultrasound were carried out using a laboratory scale mechanical flotation cell with a 20 kHz sonotrode (Sonopuls HD 200, maximum HF power P_{max}= 200W). The power level could be infinitely adjusted. The ultrasonic power applied was specified as proportionate to maximum power output of the sonotrode.

For the use of ultrasound during the reagent emulsification stage, it was found that in comparison to the reference flotation process (no ultrasound), a significant improvement on the selectivity was achieved when the reagents were irradiated continuously at a lower power level P= 0.7 P_{max} or irradiated at maximum power P= P_{max}. A specific minimum energy obtained by the combination of ultrasonic power and ultrasonic irradiation time had to be applied to obtain positive effects on the separation efficiency with ultrasonic emulsification. It was also observed that at the highest input of specific energy along with continuous ultrasonic irradiation, the separation efficiency deteriorated.

For various ultrasonic irradiation times and a constant HF power of 200 W output by the sonotrode, it was observed that better flotation results were achieved as the irradiation time increased, i.e., at a constant solid recovery in the concentrate, the ash content in the concentrate decreased. However it was also found that with lower power, the flotation results approached those of the reference (no ultrasound) flotation process. Overall, the use of ultrasound during the dispersion of the solids in the suspension was found to improve the separation efficiency of the flotation process. In other words, lower ash content in the concentrate was achieved when using ultrasound, as opposed to not using it at the same solids recovery.

At various ultrasonic irradiation times and constant ultrasonic power P_{max}= 200 W, it was observed that for constant solids recovery in the concentrate, by increasing irradiation time per stage of flotation, a lower ash content was achieved and thus the improvements compared to the reference flotation were found to be larger. Furthermore, the results indicated that with increasing power, the influence of irradiation time became more pronounced and the flotation efficiency improved. The ash content was also found to be reduced in the concentrate by either an increase in the ultrasonic power or irradiation time.

Compared to the reference flotation experiment, it was found that at the maximum ultrasonic power, $P= P_{max}=200W$, and irradiation time of 2 minutes, a decrease in the ash content by 0.6% was observed.

In conclusion, the use of ultrasound in the various stages of the fine particle flotation process, particularly during dispersion, was found to improve concentrate grade at constant solids recovery compared to flotation processes not using ultrasound. According to the authors, the disadvantages of the ultrasound process included the reduction in the flotation rate and wear on the sonotrode. In addition to these disadvantages, it was found that it was often necessary to carefully control the ultrasonic irradiation time and power within certain limits, to be able to achieve the desired high grade concentrates.

2.4.1.3 Carrier Flotation

Carrier flotation, also referred to as piggyback flotation or ultraflotation, makes use of an auxiliary mineral as a carrier for the flotation of fine particles. Carrier flotation has been used for a long time and according to Somasundaran (1979), the first commercial application of carrier flotation was used by Engelhard Minerals and Chemicals for the purification of kaolin, whereby titaniferrous impurities present in the kaolin clay were removed using coarse calcite particles as the carrier. Basically, the idea behind carrier flotation is that fine particles form slime coatings on the coarser carrier mineral, and the coated particles are then floated. Both the carrier and fine particles are made hydrophobic by the adsorption of a collector. Critical requirements for the success of the carrier flotation process include: (i) the presence of coarse particles,

(ii) carrier particles which are less than 50 μm, (iii) the use of high energy agitation, and (iv) the carrier as well as the fine particles are or are made hydrophobic (Warren, 1984). In addition to this, the carrier flotation process is dependent on a number of variables such as the intensity and time of agitation, pH, surface charge and cell geometry, and proportion of coarse to fine particles in the pulp (Subrahmanyam and Forssberg, 1990). A disadvantage of the carrier flotation process is the separation of the valuable mineral fines from the carrier mineral once flotation is complete (Singh et al., 1997). According to Singh et al (1997), however, Hu et al (1988) have examined the possibility of using the same kind of mineral as the carrier, a process known as autogeneous-carrier flotation.

Jorge and Hoberg (1993) described an experiment with a number of fine particles in which the carrier used was polypropylene particles coated with oleic acid. The results obtained from their experiment was that since the polymeric carrier particles used were of lower density than water, the actual separation by flotation was found to be rapid and allowed for an easy removal from the pulp. Detachment of the collected particles from the carrier was found to be very effective in using normal agitation in alkaline media. In addition to this, they found that excellent results were obtained for the separation of sulphides, oxides, and salt type fine materials in laboratory scale tests.

Carrier flotation focuses primarily on improving the flotation of fine valuable minerals. The procedure makes no mention on selectivity procedures to ensure that only one type of mineral is adhered to the carrier mineral while others remain in suspension. In addition to this problem as well as those mentioned by the researchers above, the procedure appears to have been used for only a small number of minerals.

2.4.1.4 Dissolved Air Flotation (DAF)

Dissolved air flotation is a procedure used for removing fine suspended material from an aqueous suspension. The dissolved air flotation allows for the formation of very fine bubbles which improve the flotation of fine particles (KomLine-Sanderson, www.komLine.com/Products_Services/Wastewater/DAF.htmL#anchor1892420, 2001)

Traditionally, the dissolved air flotation technique has been widely used for the treatment of industrial effluents. However, recently the process has found its way into waste treatment and in the metallurgical and mining fields for mineral fines and ultrafines separation. In general, bubbles are formed by a reduction in pressure of water pre-saturated with air at pressures higher than the atmospheric pressure. The resulting supersaturated water is then forced through needle valves or orifices, producing a cloud of bubbles ranging from 0.01-0.1 mm in diameter (Jorge, 2001). The main advantage of the DAF process is that it provides more of a positive attachment between air bubbles and the particles that are to be removed. With smaller bubbles being produced, the bubble/particle collisions are higher as described earlier. The high cost associated with the water saturation required for bubble formation has been a disadvantage of the process for a while. However Jorge (2001) argued that it has been shown that at working pressures lower than 2-3 atm, bubble generation is possible. Furthermore at this low pressure, it has been determined that very low concentrations of surfactants or collectors are required to make DAF feasible, thereby reducing drastically the cost of energy and optimizing the process. In addition to this disadvantage, fine bubbles are non-selective towards fine particles, and as a result these fine bubbles can lead to increased entrainment of fine hydrophilic particles which in turn would lower the concentrate grade.

2.4.1.5 High Temperature Conditioning

The use of high temperature (60-80^{0}C) conditioning in froth flotation, although not discussed much in various literatures, has been found to have beneficial effects on flotation of particles in the fine size ranges. Song and Lu (1989) have argued that the reason behind the improvement in flotation as a result of high temperature conditioning is that the high temperature: (i) enhances the adsorption and the kinetics of the adsorption of collectors, (ii) provides better selectivity due to the increased frothability, and (iii) allows for surface modification. In addition to this they argued that high temperature conditioning improves selectivity due to enhanced froth drainage. Since not much work has been done using high temperature conditioning, the exact effectiveness of this technique is unknown.

2.4.1.6 Split Conditioning and Combined Flotation (SCCF)

Singh et al. (1997) have reported on work they performed using the SCCF process for the enhanced recovery of values from feed containing a high percentage of ultrafine particles. The process involves a split conditioning of coarse and fine fractions under their optimum process conditions separately, followed by combined flotation in the same cell. The efficiency of the process has been demonstrated for the flotation of slimy rock phosphate ore consisting of 47.3% particles below 8 microns. The separate conditioning of the coarse and fine fractions may prove beneficial in some instances; however, given that a number of selective reagents already exist and that dispersion is used prior to the addition of these selective reagents, split conditioning and combined flotation may not be a necessary technique in many cases and for many flotation systems. Furthermore, the technique failed to address how fine gangue particles are handled.

2.4.2 Techniques Based on Equipment Design

2.4.2.1 Column Flotation

Perhaps the fastest growing technology for the flotation of fine particles is the use of column flotation cells. Although column flotation existed for many years, it was not until the early eighties that there was an ever growing interest in the technique (Dobby and Finch, 1990). A vast majority of mineral processing industries are now making use of column flotation cells, so that it would be difficult to discuss all the various types of column flotation cells that have been evolved most recently.

Column flotation employs a countercurrent flow of feed slurry and air bubbles, and has proven to be one of the most promising processes for the recovery of fines. Furthermore, the technology consists of a provision for cleaning the froth, resulting in an appreciable enhancement in the grade of the concentrate against the conventional flotation cell. The disadvantage of the column flotation cell is that recovery is low (Singh et al., 1997).

2.4.2.2 Leeds Column Cell

The use of the Leeds Column flotation cell dates back to the late 1950's where it was initially utilized as a metallurgical test device. Comparative metallurgical performance demonstrated the potential for the Leeds Column to achieve significant improvement in product grade while retaining recovery levels comparable to conventional flotation machines. Such a success led to the commercialization of the Leeds Column by WEMCO in 1988-1989 (Denger and Person, 1991) The Leeds column cell is a flotation cell containing about three to eight barrier rods which are positioned above the impeller mechanism in the cell. The purpose of these barrier rods is to delay bubbles rising in the column in the froth phase, resulting in improved mechanical drainage of entrained gangue particles and hence higher selectivity (Denger and Person, 1991). Although the Leeds Column cell is one of the few techniques which address the problems of entrainment, its success cannot be guaranteed for many mineral flotation systems since the possibility of entrapment of the gangue particles in the valuable particles can go undetected by the barrier rods, particularly if the valuable and gangue particles are of the same size.

2.4.2.3 Packed Column Cell

The packed column cell was created by an inventor named Yang (Singh et al., 1997). The idea behind this technology is that it uses stacks of corrugated plates which provide a very tough route for the bubbles and fine particles to go through, thus reducing mixing. As the technology was still new at the time at which Singh et al (1997) discussed it in their article, results from the use of this technology were not included. However, the packing of this cell was expected to help in dispersing the gas in the absence of spargers and control the unlimited froth depth for fine particle cleaning (Singh et al., 1997).

2.4.2.4 Jameson Cell

One of the accepted technologies for improving the flotation of fine hydrophobic particles is the Jameson cell, developed by Professor Jameson himself in 1985. The first production Jameson cells installed in 1989, were lead cleaner units at Mt Isa (Xstrata Technology, 2004). The installation reveals a big difference in flotation rates between the Jameson cell, mechanical cells, and flotation columns. Figure 3 (Xstrata Technology, 2004), illustrates a typical Jameson flotation cell.

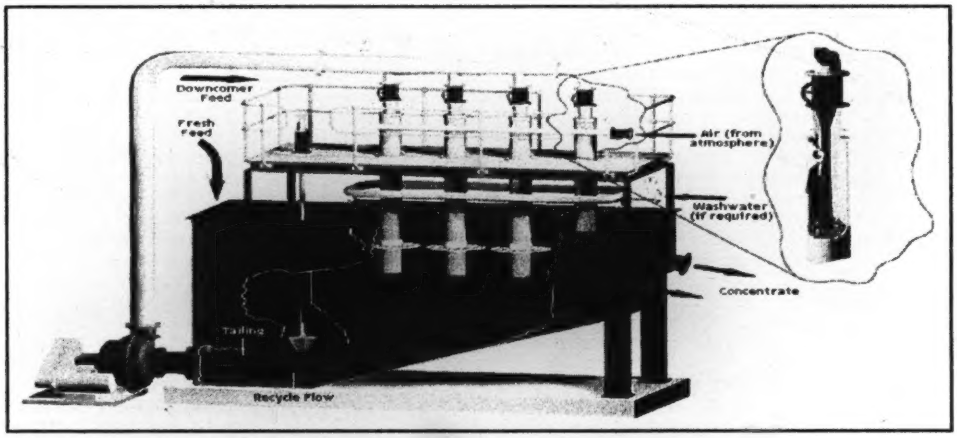


Figure 3: The Jameson Cell (Xstrata Technology, 2004)

Basically in the Jameson cell, the central portion of the conventional column cell is replaced by a downcomer. The feed slurry is forced through a nozzle forming a jet of slurry which then draws air into the central downcomer. The aerated slurry is discharged into a tank and the froth formed is washed by jets of water and collected in the concentrate launder. Unlike mechanical or column flotation cells that are residence time dependent, the Jameson cells are contact dependent. The two main zones of the Jameson cell consist of the contacting zone and the cleaning zone. In the contacting zone, contacting or particle collection take place in the vertical downcomer where the air and pulp are intimately mixed inside this downcomer. The efficiency of the Jameson cell is the result of the intense mixing in the confined spaces of the downcomer as well as the very fine bubble sizes that are formed. The dense mixture of bubbles and pulp are discharged at the base of the downcomer where they enter the quiescent outer portion of the cell. Disengagement of the air bubbles from the pulp then occurs which causes the air bubbles to rise into the froth layer. A high purity concentrate is collected and overflows, while the bubble-free pulp discharges from the bottom of the cell as tailing (Harbort et al., 1994). Some of the advantages of this technology include: high performance, low cost, no moving parts, and the production of small bubble sizes which are beneficial to fine particle flotation (Xstrata Technology, 2004). Mechanical entrainment due to the production of fine bubbles is likely to occur by using the Jameson cell making this a disadvantage of this technique.

2.4.2.5 Hybrid Cells

Hybrid cells were developed by Outokumpu, and are also referred to as the High Grade machines (Koivistonen and Kunnitinen, 1991). The first prototype of the machine was used in a copper cleaning circuit in a mine in Finland in 1989. The technology combines both the characteristics of a conventional mechanical flotation cell with an arrangement of froth washing in a deep froth layer. The top part of the machine consists of a column forming a 0.5 m froth layer. Wash water is sprayed through nozzles 5-15 cm down the froth layer. The main advantages of these hybrid cells are that they can replace three conventional cleaning stages with one, thus producing purer concentrates with high recoveries (Singh et al., 1997). In addition to this the cell can deal with the low recoveries of coarse particles which are common with column flotation cells. Due to the additional components required for the hybrid cells, however, it would most likely be costly for industries to utilize such technology on a large scale. This is perhaps a main disadvantage of the hybrid cells technology.

2.4.2.6 Air Sparged Hydrocyclone Flotation (ASH)

Air sparged hydrocyclones combine the froth flotation technology with the flow characteristics of a hydrocyclone, leading to a fast separation of minerals. In this system, the ore slurry is fed tangentially through a conventional cyclone into porous cylinder. This causes a swirl flow motion in a radial direction, which is discharged through the annular opening located at the bottom of the ASH. Air is then sparged through the jacket porous cylinder which allows the bubble/particle attachment. With a reduction in the tangential velocity of hydrophobic particles these particles are transported with the bubbles into the froth phase and discharged as the overflow product. The hydrophilic particles are discharged as the underflow product (Miller and Ye, 1989). The machine is capable of a fast flotation rate along with a high capacity. In comparison to the conventional mechanical cell, the ASH has better selectivity.

2.4.2.7 Rapid Flotation System

Developed by the United States Bureau of Mines, the rapid flotation system consists of two components, namely: the bubble attachment unit and the pulp-froth separator. The ore slurry is mixed with the bubble slurry under high turbulent conditions. The bubble slurry mixer is then transferred to a quiescent shallow depth froth separation unit. In this unit the mineral laden air bubbles are separated while tailings are discharged from the conical bottom of the separator. Compared to a conventional mechanical cell, the kinetics of flotation is more rapid in the rapid flotation cell (Jordan, and Susko, 1992). Based on the description of this technique, it appears as though there is minimal selectivity using rapid flotation. In other words the probability that fine hydrophilic particles are attached to the bubbles is probably the same as that for the fine hydrophobic ones; thus entrainment is not controlled using this technique.

2.4.3 Techniques Based on Reagent Design

2.4.3.1 Chemisorbing Flotation Collectors

Various researchers have discovered that chemisorbing type collectors can be used in the flotation of fine ores containing slimes. Singh et al. (1997) have claimed that Fuerstenau (1980) attributed this improvement in the recovery of fines to a number of reasons, namely: (i) lower reagent consumption due to the free energies of chemisorption (ii) higher selectivity even at finer sizes due to specific chemical interaction between collector ion and metallic cation on the mineral surface, and (iii) better recovery of fine particles due to the reduced adsorption of collector on air bubbles. Singh et al. (1997) observed that by using potassium octyl hydroxamate as a collector, there has been an enhancement in copper recovery from oxidized copper sulphide ore containing a high percentage of fines. Collectors in general have been found to be successful in rendering certain minerals hydrophobic and thus allowing for their recovery into the froth. Using collectors alone may guarantee a high recovery of a particular mineral; however, the grade of that mineral may suffer due to the entrainment of unwanted gangue minerals into the froth. In order to prevent such an occurrence from taking place, a depressant would have to be added to selectively adsorb onto the surfaces of the gangue particles. The mechanisms through which a depressant functions will be discussed.

2.4.3.2 Addition of Collector Before Grinding

The addition of a collector before the grinding stage was found to significantly improve the flotation of fine hydrophobic particles. The early addition of the collector was said to prevent the surface of the floatable hydrophobic minerals from reacting with hydrophilic ions. Thus the floatability of the fine hydrophobic minerals is remarkably increased (Smith and Warren, 1989).

2.4.3.3 Extender Flotation

Capponi et al. (2003) conducted an experiment involving the use of a technique known as extender flotation. The objective of their study was to compare standardized flotation copper sulphide mill tests with flotation techniques based on oil extender using emulsified oils. Copper porphyry samples, containing about 37% of the total copper content in the fines and ultrafines fractions, were used in their work. Lime was used as the pH regulator to maintain the froth solution to about a pH of 10.5. The frother used was a mixture of DF 250, MIBC (methylisobutyl carbinol), and pine oil. Diesel and kerosene were used as the extender oils.

The standardized flotation tests were carried out in a 3 L laboratory Denver D12 cell. The feed (38% solids content, pH 10.5) was conditioned at 1000 rpm for 3 minutes to allow sufficient collector and frother adsorption. Concentrate samples were collected at 1, 3, 5, 7, and 9 minutes. The samples were then dried, weighed, and analyzed for copper by atomic absorption.

For the extender flotation tests, kerosene and diesel-in-water emulsions were prepared in a high free rotational speed stirrer for 10 minutes. The extender oils were used as an extra reagent added after the collector and frother addition during the conventional conditioning. The oil concentrations were 30, 60, 90, and 120 mg/L. The oils were added at the desired pH of 10.5, and the oil to water volume ratio was kept at 1:99. After the emulsion additions, the flotation procedure proceeded similar to that of the standard mill flotation test.

The results from the test indicated that by using the extender flotation technique, concentrate recoveries were increased about 3-5% in true flotation recoveries, and between 20-30% in flotation rate. The reason for this improvement in the flotation of these fine particles was attributed to enhanced hydrophobisation and aggregation of the fines with themselves or with coarser particles (carrier). Thus the extender flotation technique was found to be beneficial in improving the floatability of fine hydrophobic particles.

2.4.4 Methods for Examining and Reducing Entrainment during Flotation

Much of the recent work examining fine gangue particle flotation involved studying the froth layer as well as producing models of flotation cells to determine ways that could be used to minimize mechanical entrainment. The efficiency and selectivity of the froth flotation process depends on a variety of factors, such as the size of the minerals and bubbles, the depth of the froth, the rate of concentrate removal, and the aeration rate. In general, true flotation of valuable mineral particles attached to the surfaces of bubbles determines the efficiency of the process. On the other hand, it is the degree to which unwanted gangue particles are entrained with water that determines the selectivity of the flotation process (Ross, 1990). In trying to produce models of what specifically takes place in the flotation froths, it is crucial to have rough estimates of the contributions made by true flotation and entrainment.

The majority of the studies of the froth phase in flotation revolved around the separation of the various species involved in the flotation process and their transfer from the froth to the concentrate, as well as on the pulp-froth transfer of solids and water. One of the earliest works involving froth research was carried out by Bisshop and White (1976). By specifying two parameters, Bisshop and White were able to determine the rate of recovery of hydrophilic particles into the concentrate. The conclusion drawn from the work of Bisshop and White was that residence time in the froth was the single most important factor in drainage from the froth. Bisshop and White made no mention of the use of polymeric depressants to minimize the entrainment of the fine hydrophilic gangue particles and so such conclusions may have varied had they done so.

Laplante et al. (1983) used a special constructed flotation cell with a high cell height-to-froth surface ratio, in which two zones of different activity were formed in the pulp phase to examine the effects of air flowrate and frother concentration on the flotation rate of different size classes of quartz and galena. Impeller action in the lower part of the cell was used to suspend the particles, whereas in the top part which was only weakly agitated, a quiescent slurry-froth interface ensued. This method resulted in negligible entrainment, permitting the rate of true flotation to be examined. The problem with this method is that it would most likely be costly to manufacture such flotation cells and more tests would probably be required to verify its effectiveness. In addition to this disadvantage, the particle sizes of the minerals were all greater than 10 μm and so entrainment was not much of a problem to begin with.

In an attempt to fully understand entrainment, most recently Neethling and Cilliers (2002) have described a model known as the general froth simulator (UMIST FrothSim), which allows the modeling of a wide range of flotation conditions since it takes into consideration a large number of the physical phenomena that occur within the flotation froths. The model was designed to explain the observed entrainment and collection of the gangue. Plateau borders were used in the model as drainage channels for hydrophobic solids. In developing the model, the first stage was to model the various parameters of the flotation process such as gas and liquid motion as well as the solids motion. When modeling the solids motion, it was assumed that the solids in the froth fall into one of two types, the particles that are attached to the bubbles and are assumed to be hydrophobic and the particles that are unattached and free to move which are considered to be a result of non-selective entrainment from the pulp into the froth as well as from hydrophobic particles which detach from the bubbles.

Equations that were manipulated and used in the model showed that the vertical flux of the gangue at any point is a result of three factors: the upward motion of the liquid, the downward settling of the particles under gravity, and the dispersion of the solids. A plot of froth height versus solids concentration at the plateau borders for 10 μm particles showed that as the air rate increased in this model, there was an initial decrease in gangue concentration at the plateau borders with increase in froth height due to the initial rapid drop in water content of the froth directly above the pulp-froth interface. After this initial change, there follows a large range of froth depths through which there is, for a wide range of air flowrates, little change in gangue concentration with height. It was also found that the effect of dispersion is negligible for a significant portion of the froth height. As a result the balance between the upward motion of the liquid and the hindered settling of the solids primarily determines the motion of the gangue through this region. Such an observation results in a linear relationship between the water and gangue recovery.

Overall, the FrothSim model was found to accurately predict the gangue-water recovery trends that have been found experimentally. Furthermore, it has been found to be useful to explain entrainment results previously obtained on the basis of particle dispersion and liquid transport. It can, therefore, be concluded that the results from this model can be used to guide practical recommendations for minimizing entrainment and increasing grade in the future. Accuracy of this method relies largely on flotation conditions
The effectiveness and efficiency of the flotation process depend not only on chemical variables such as the types of the reagents or the pulp pH, but also on the hydrodynamic conditions within the flotation cell (Cilek and Yilmazer, 2003). These hydrodynamic parameters relate directly to many sub-processes of flotation, such as the suspension of particles in the pulp, dispersion of air into bubbles, and the probability of particle-bubble collision. Numerous dimensionless groups such as Reynolds number, Froude number, and Weber number have been used to characterize the hydrodynamics of flotation cells. These dimensionless groups are defined by some physical variables such as pulp density, impeller speed, and aeration rate. The physical variables in turn are related to water recovery and gangue recovery, i.e. mechanical entrainment.

Cilek and Yilmazer (2003) studied how gangue entrainment and flotation performance respond to changes in physical variables and how they can be accurately predicted with a multivariable non-linear model and a neural network model. The multivariable non-linear model was basically a six-factor, two-level, factorial design, which allowed the study of six variables with only sixteen runs (tests). The six variables chosen as factors were: volumetric flowrate of air, impeller speed, pulp density, froth thickness, frother concentration, and flotation time. The material used was a copper ore. Results from this experiment indicated that air flowrate and flotation time had a significant effect on the copper and water recovery, which was a typical characteristic of entrainment. Froth thickness, on the other hand, had the highest effect on the grade of the concentrate. The authors also stated that the main disadvantage of the multi-variable non-linear model is that the identification of the sub-flotation processes, and the corresponding cause and effect relationships, is extremely difficult due to the complex interactions between physical and chemical parameters.

Although the models discussed in this section are relevant in the sense that some flotation parameters can affect entrainment to a certain degree, much of the findings from using these models such as the relationship between the recovery of water and entrainment are already known facts. Factors such as the type and amount of minerals used, the type and concentration of reagents used, and the type and geometry of the flotation cell used may actually produce results which vary from the actual findings of these models.

2.5 Commentary on Previous Work Done

Most of the work discussed in section 2.4 pertains mainly towards improving the flotation of fine hydrophobic particles with little regards towards minimizing the entrainment of the unwanted fine hydrophilic gangue particles. Much research has been done to indicate that the small mass and high surface areas of fine hydrophobic particles are the main reasons as to why hydrophobic particles are not easily floatable. The problem with such techniques though is that they tend to ignore the inevitable fact that due to their small sizes, the presence of fine hydrophilic particles in a flotation pulp will always pose the problem of mechanical entrainment which will in turn lower the grade of the concentrate. In fact, as long as fine hydrophilic particles remain dispersed in a flotation pulp, using techniques that improve the flotation of fine hydrophobic particles while neglecting the presence of the fine hydrophilic particles will almost always aggravate entrainment. Although some of the methods in section 2.4 claim to minimize entrainment, many of these techniques are either too costly to employ or lack enough experimental results to justify these claims. In addition to this argument, the use of polymeric depressants to minimize entrainment has not been mentioned in any of these techniques.

2.6 General Theory of Particle Interactions

The combined effects of pH and reagents used for a specific mineral influence particle behavior in terms of whether the particles combine to form flocs or whether they remain well dispersed. Particle charge resulting from these combined effects, as well as the electrolyte charge is the main determinant in such particle behavior. Particle coagulation, flocculation, or dispersion are the three types of patterns observed in flotation.

2.6.1 Particle Coagulation

Particle coagulation occurs when extremely fine colloidal particles adhere directly to each other. In general, particles exert mutual attraction forces known as Van der Waal's forces which are effective only at very close range. An obstacle to the Van der Waal's forces typically results from the presence of an electrically charged atmosphere around each particle which generates forces between particles approaching one another. In any given system the electrical charges on the particle surfaces will be of the same sign and will generally be negative, particularly in aqueous suspensions of pH 4 and above (Wills, 1997). Repulsion forces exist between the particles due to the presence of the same sign on each particle and, therefore, not only prevent the coagulation of the particles, but also keep the particles dispersed. In order to overcome these repulsion forces, ions with the opposite charge to that present on the surface of the particles in suspension would have to be added to the solution.

Coagulants are electrolytes whereby an ion having an opposite charge to particles in a suspension are adsorbed and therefore result in charge neutralization when dispersed in a system, which in turn allows particles to adhere to one another. Particles that have a zero charge in relation to the suspending medium (i.e. zeta potential is zero), produce the most pronounced coagulation. Inorganic salts containing highly charged cations such as Ca^{2+} and Fe^{3+} are typically used as coagulants (Wills, 1997).

Zeta potential measurements provide an understanding of coagulation behavior. A negatively charged particle suspended in solution will attract positive ions from that solution to form a bound layer of positive ions which is known as the Stern layer. A diffuse layer of counter ions will also be formed. The counter ions in the diffuse layer decay in concentration with increasing distance until solution equilibrium is attained. These two layers of ions close to the surface constitute the electrical double layer. As the particle moves in the liquid, shear occurs between the Stern plane which moves with the particle, and the diffuse layer. The potential at this shear plane is the zeta potential and is dependent on the surface potential and the concentration and charge of the counter ions. Thus it can be seen that the greater the counter-ion charge and concentration (within limits in order to avoid charge reversal), the lower the zeta potential and as a result coagulation becomes easier (Rajagopalan, 1997).

2.6.2 Particle Flocculation

Particle flocculation involves the formation of much more open agglomerates than those resulting from coagulation and relies upon molecules of a reagent acting as bridges between separate suspended particles. Reagents used to form these "bridges" are long chain organic polymers such as starch and guar gum. In order for bridging of particles to occur, the polymer must be strongly adsorbed and this is made possible by chemical groups having good adsorption characteristics. Bridging flocculation occurs when a segment of a very long molecular chain of a flocculant is adsorbed on the surface of a particle, leaving a large proportion of the chain free to be adsorbed on another particle, therefore forming an actual molecular linkage or bridge between particles. The efficiency or strength of adsorption of the polymer on the surface, the degree of agitation during flocculation, and the subsequent agitation, which can result in breakdown of flocs are all factors which play a role in the degree of flocculation (Wills, 1997).

The term selective flocculation is often used in flotation and refers to specifically flocculating the desired minerals in a pulp, followed by separation of the newly formed aggregates from the dispersed material. In order for selective flocculation to be successful, the minerals in the pulp have to be dispersed prior to the addition of a high molecular weight polymer, which selectively adsorbs on only one of the constituents of the mixture (Wills, 1997).

2.6.3 Dispersion

When particles of a mineral are neither flocculated nor coagulated to one another, nor even to particles of an alternative mineral (i.e., hetero-coagulation), they remain in a state known as dispersion. A stable system is a system whereby all the particles are well dispersed and remain that way. Once coagulation or flocculation of particles occurs, the suspension becomes unstable. Dispersion is crucial in flotation as it allows for the selective adsorption of reagents such as depressants and collectors on various minerals within a given flotation system. Examples of typical dispersants include sodium silicate and sodium metaphosphate. Dispersants typically function by removing coagulants from a flotation pulp, thus increasing the double layer repulsive forces between particles (Arol and Iwasaki, 2003).

2.7 Flocculation Characteristics of Various Minerals

2.7.1 Hematite and Hydroxylapatite

Starch, particularly corn starch has been used for many years as a universal gangue mineral depressant (Araujo et al., 2005). The basic composition of starch is $(C_6H_{10}O_5)_n$, the number n of D-glucose units being higher than one hundred (Pinto et al., 1992). The two major components of starch are amylopectin and amylose. Amylopectin is a branched polymer in which the main chain is linked to the branches through α-1,6 glucosidic bonds. On the other hand amylose is a linear polymer showing D-glucose units linked by α-1,4 glucosidic bonds (Peres and Correa, 1996). Weissenborn (1996) examined the behavior of these two starch components in the selective flocculation of iron ore and high purity hematite, and found that amylopectin flocculated the bulk of the iron ore and hematite while amylose failed to flocculate any minerals. When both these starch components were combined, it was found that amylose suppressed the ability of amylopectin to flocculate the bulk of the iron ore and slightly enhanced the selective flocculation of hematite. According to adsorption experiments conducted, amylopectin was shown to have a greater affinity for hematite and adsorption density on hematite compared to amylose. Weissenborn (1996) concluded that the superior flocculation and adsorption ability of amylopectin was attributed to its larger molecular weight and branched structure. This behavior was especially evident at pH 10.5. Pinto et al (1992) have observed similar findings with regards to the effects that each of the two starch components had on hematite. Iwasaki et al (1969), however, reported that according to extensive studies conducted by Chang et al (1953), amylose showed better selectivity than amylopectin for oxidized iron ores.

Corn starch contains 75% amylopectin and 25% amylose (Weissenborn 1996). According to the work of the researchers mentioned in this section, this 3:1 ratio of amylopectin to amylose in corn starch may well explain why corn starch is an effective depressant.

Peres and Correa (1996) have reported that among the depressants used in flotation plants in Brazil, corn starch played a relevant role in iron oxide depression in the reverse cationic flotation (amine employed as collector) of itabiritic ores. Weissenborn et al, (1994) carried out a laboratory scale selective flocculation process for recovering iron oxide from a sample of ultrafine iron ore tailings containing kaolinite as the main gangue mineral. The objective of their work included selecting an appropriate flocculant and optimizing parameters that affect selectivity and recovery. The findings of Weissenborn et al (1994) were that wheat starch was found to be a superior selective flocculant for flocculating the hematite. Other findings included the fact that the concentrate grade of all minerals was insensitive to changes in the selective flocculation conditions; however, the recovery of all minerals was sensitive to changes in the selective flocculation conditions. The optimum conditions included using a pH of 10 to 10.5 and a flocculant concentration of 50 mg/L (ppm).

Arol and Iwasaki (2003) studied the effect of sodium silicate on the flocculation of hematite with starch in the presence of calcium. Sodium silicate is a widely used dispersant in many mineral processing applications, including the selective flocculation of iron oxides to disperse quartz (Arol and Iwasaki, 2003). Studies with quartz have shown that the method of dispersion with sodium silicate is due to its ability to remove the coagulating constituents such as calcium and magnesium ions from mineral surfaces and then form silicates of these cations thus reducing their concentrations as free ions. In addition to this it is argued that sodium silicate can behave as an effective dispersant only when the concentration of calcium is low. This is due to the fact that above a certain concentration of calcium, more sodium silicate would be needed which would result in the dispersion of iron oxide even in the presence of starch. The dispersion would occur due to the newly formed calcium silicate precipitates shielding the adsorption of starch on hematite. Montes-Sotomayor et al. (1998) conducted reverse flotation tests involving the flotation of quartz particles and the depression of hematite particles using corn starch. Montes-Sotomayor et al.(1998) observed that starch normally adsorbs specifically on both minerals. However, in the presence of an alkaline medium (pH 10), the starch had desorbed from the quartz in the presence of an amine collector, whereas for hematite, the starch-mineral affinity remained the same. The results was that the hematite was depressed while the quartz was floated.

The use of corn starch for the flocculation of apatite has also been used for a number of years. According to Guimaraes et al. (2005), starch depresses apatite more effectively than calcite despite the fact that both minerals are sparingly soluble and contain the same cation (Ca^{2+}). Others such as Sis and Chander (2003) and Henchiri (1993) only report the success of starch as a depressant for apatite, but did not provide detailed data.

None of the above mentioned authors in this section have discussed the relationship between fine particle size and entrainment when mentioning the use of starch as a depressant. In fact all the minerals used in their work were larger than the critical size range where entrainment dominates and poses a problem. In other words the authors have only discussed the froth flotation process, where depressants are used mainly for the purpose of selectively separating the gangue minerals from the valuable minerals with no reference being made to the use of depressants for minimizing entrainment of fine gangue hydrophilic particles.

2.7.2 Quartz

Quartz is a typical mineral encountered in flotation. In reverse flotation procedures, quartz is the mineral to be floated. The use of amine collectors in flotation dates back to almost one hundred years. Scott and Smith (1992) examined the effect of various amine collectors on the flotation of quartz and magnetite. Based on their findings, amines were observed to be stronger collectors for quartz than for magnetite. In addition to this finding, among the various lengths of carbon chains in the various amine collectors, it was found that the longer the chain length, the better the flotation at a set amine concentration. Finally Scott and Smith (1992) observed that the 12 carbon diamine is a stronger collector than a 12 carbon monamine.

3 OBJECTIVE

Work is currently being done, whereby polymeric depressants are used to create hydrophilic flocculation in conjunction with hydrophobic flocculation (Liu, 2003). By doing this it may be possible to keep mechanical entrainment to a minimum, while at the same time maintain a high recovery of the hydrophobic particles. Three slightly different methods can be used in which hydrophilic flocculation in conjunction with hydrophobic flocculation can be performed. The first step in all three methods involves dispersing the minerals in the flotation pulp with an effective dispersant such as sodium silicate to prevent hetero-coagulation of the various minerals from occurring. All three methods are concluded by froth flotation as the procedure for separating the valuable minerals from the gangue minerals. The first proposed method involves the use of shear flocculation, oil agglomeration, or carrier flotation to allow the hydrophobic flocculation of the valuable mineral after adding a suitable collector, followed by the addition of a polymeric depressant to allow the hydrophilic flocculation of the fine gangue particles.

The second proposed method which is the method examined in this research, involves the addition of a polymeric depressant to the pulp containing the dispersed minerals to cause the hydrophilic flocculation of the fine gangue mineral. A collector would then be added to float the valuable mineral.

The final proposed method is very similar to the second one; however, after hydrophilic flocculation, primary collectors and other auxiliary collectors (hydrophobic polymers, latex, oil, etc.) are added to induce hydrophobic flocculation.

The objective of this research project was to verify that the mechanical entrainment of hydrophilic particles is positively correlated to particle size, and to examine the effect of polymeric depressants such as starch on increasing the particle sizes of these hydrophilic particles so that their entrainment can be minimized. Using hydrophilic and hydrophobic flocculation in conjunction with one another was also examined. The scope of the research was limited to laboratory-scale equipment.

4 EXPERIMENTAL

4.1 Minerals Used

Table 2 lists all of the materials that were used in the tests carried out in this research

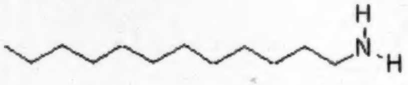
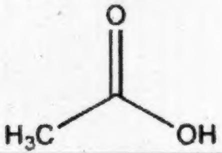
Table 2: Minerals used in Research

Material	**Particle size**	**Supplier**
High purity Iron(III) Oxide (Hematite)	$d_{50} = 2.5$ µm	Aldrich Chemicals
Hydroxylapatite ($Ca_5(OH)(PO_4)_3$)	$d_{50} = 6.4$ µm	Fisher Scientific
High purity quartz crystals (SiO_2) (Hot Springs Arkansas)	-74+38 µm	Ward's Scientific
Fine Quartz (SiO_2)	-20 µm	Boud Minerals & Polymers, U.K
Sphalerite (ZnS)	-38 µm	Ward's Scientific
Galena (PbS)	-38 µm	Ward's Scientific

4.2 Reagents

Table 3 lists all of the reagents used in this research along with their function and the supplier.

Table 3: Reagents used in Research

Reagent	Function	Supplier
Corn starch	Depressant	Sigma Chemicals Co.
Corn Dextrin	Depressant/Dispersant	Sigma Chemicals Co.
Carboxymethyl cellulose (CMC), M.W = 80,000	Depressant	Polysciences, Inc.
Carboxymethyl cellulose (CMC), M.W = 700,000	Depressant	Polysciences, Inc.
Sodium Metaphosphate	Dispersant	Fisher Scientific
Sodium Silicate	Dispersant	Fisher Scientific
Nitric Acid	pH modifier	EM Science
Sodium Hydroxide	pH modifier	Fisher Scientific
Dowfroth 250	Frother	Dow Chemicals
Dodecylamine 	Collector Ingredient	Sigma Chemicals Co.
Acetic Acid 	Collector Ingredient	Sigma Chemicals Co.

4.3 Reagent preparation

4.3.1 Corn Starch and Dextrin Stock Solutions

The procedures for preparing the corn starch reagent described in this section involved the preparation of a 1g/L stock solution. In fact stock solutions for most reagents used in this research were prepared at this concentration (1 g/L).

On a Denver Instrument Company TR-104 scale, 0.1 g of Sigma S-4180 corn starch powder was weighed out on a piece of paper. The powder was then transferred to a beaker where a few drops of distilled water were added and mixed with the powder to form a paste using a stirring rod. About 50 mL of boiling distilled water was then added to the beaker containing the paste and with the use of the stirring rod, the solution was stirred gently until the paste was well dispersed in the solution. The corn starch solution was then transferred to a 100 mL volumetric flask where distilled water was added until the water level reached the 100 mL mark. Since it was difficult to fully dissolve the corn starch in the solution (this was seen by the fact that the solution was milk cloudy in appearance), 1 g of NaOH pellets was added to the stock solution in the flask to help dissolve the corn starch. The solution in the flask was left to stand for about 15-20 minutes until it became clear. The sealed flask was then inverted and gently shaken a number of times to ensure the starch in solution was evenly dispersed. Since corn starch has a tendency to degrade, it was important to prepare the solution daily.

The procedure used in preparing the corn starch stock solution was also used in preparing the dextrin stock solution. However, since dextrin dissolves much more easily than corn starch, NaOH pellets were not added.

4.3.2 Carboxymethyl cellulose (CMC, M.W= 80,000 and 700,000) Stock Solutions

The procedures for preparing the carboxymethyl cellulose (CMC) solutions, both of molecular weights 80,000 and 700, 000, were identical to each other. Once again 1 g/L stock solutions were prepared.

A beaker containing about 50 mL of distilled water was placed on the Corning stirrer/hot plate. The heater was then turned on and adjusted to a medium setting so that the water was warm enough to speed up the dissolving process but at the same time prevent the water from actually boiling. One tenth of a gram (0.1 g) of CMC was then sprinkled slowly into the warm water in very small increments every 5-10 seconds while stirring. This process was continued until all of the powder was added and dissolved. The resulting viscous solution was then transferred to the 100 mL volumetric flask and the beaker was rinsed a number of times to ensure that all of the solution was transferred from the beaker to the flask. Additional distilled water was then added to top the solution to the 100 mL mark. The flask was then sealed and inverted a number of times. The CMC 700K stock solution appeared much more viscous than that of the CMC 80K.

4.3.3 Dispersant Preparations

The two main dispersants used in this research were sodium metaphosphate and sodium silicate. Preparation of both these dispersants was simply done by dissolving 0.1 g of the dispersant of interest in 100 mL of distilled water and inverting the sealed flask a number of times. If necessary, an ultrasonic bath was used to aid in dissolving the solids.

4.3.4 Collector Preparation

The sole collector used in this research was dodecylamine acetate (DDA). The concentration of the stock solution of this collector to be prepared was 10^{-3} mol/L. Since the molecular weights of acetic acid and dodecylamine are 60.05 g/mol and 185.4 g/mol, respectively, and the total stock solution volume to be prepared was 1 L, in order to prepare a 10^{-3} mol/L solution, 0.06005 grams of acetic acid and 0.1854 grams of dodecylamine were to be combined together. In order to do this 0.1854 grams of dodecylamine solids was added to a beaker containing approximately 150 mL of warm distilled water placed on top of the Corning stirrer/hot plate. The solution was then gently stirred and 0.06005 grams of acetic acid was added to the beaker. Once all of the dodecylamine particles were dissolved, the contents of the beaker were transferred to a 1000 mL volumetric flask and distilled water was added to the one liter mark. The flask was then sealed and inverted for about ten times at which point the collector formed would start to foam indicating a well prepared collector stock solution.

4.4 Settling Tests Procedures

The purpose for carrying out settling tests was to determine the degree of flocculation of the various minerals by the addition of various depressants and dispersants. Minerals that were well flocculated using a depressant would settle faster than those that were dispersed by either adding no reagent or adding a strong dispersant. The first step in the procedure for this portion of the experiment was to weigh out a given amount of solids of the mineral to be tested (5 grams for hematite and hydroxylapatite, and 2 grams for quartz and sphalerite) and place the solids in a 250 mL beaker. Approximately 150 mL of distilled water was then added to the beaker and the beaker placed on top of the Corning stirrer/hot plate. The pH of the solution was then adjusted to a specific value of interest using a few drops of either 0.1N NaOH or 0.1N HNO_3.

The next step was to add the reagent of interest in the desired concentration using a 10 mL pipette. If necessary, the pH would once again be adjusted to the desired value since some of the additives such as corn starch would drastically change the pH. Stirring the contents of the beaker was continued for an additional three minutes to allow proper conditioning of the reagents on the materials prior to pouring the contents of the beaker into a 250 mL volumetric cylinder. Any solids remaining in the bottom of the beaker were rinsed with distilled water into the cylinder. Additional distilled water was then added to top the water level in the cylinder to the 250 mL mark. In general, regardless of the concentration of the reagent used, it was important to ensure that the total solution level in the cylinder was maintained at 250 mL for each test. If, for example, the concentration of an additive required was 50 ppm, of this 250 mL, the reagent concentration would account for 12 mL of the total and 238 mL would be the total distilled water used. The cylinder was then sealed, inverted and shaken for eight times. Once this step was completed, the glass cork used to seal the cylinder was removed, and the cylinder was quickly placed under a pipette attached to a vacuum system. The pipette was immersed into the cylinder such that the bottom tip of the pipette was evenly leveled with the 50 mL mark of the cylinder. A stopwatch was then immediately started, and the solids in the cylinder were allowed to settle for a given period of time which was determined by trial and error for each mineral. Upon completion of each settling test, the vacuum was turned on and the entire solution above the 50 mL mark was siphoned out of the cylinder (200 mL in total). The remaining solution was then filtered of its water content, and the solids on the filter paper were dried. Once dried the solids were removed from the furnace where they were exposed to the atmosphere overnight. The next day the dried settled solids were weighed, and the percent of settled solids calculated. In this portion of the experiment, it was important to record the exact weight of the solids used prior to the start of each test since calculating the percent settled solids was based on this value. The procedure was repeated for each mineral tested using a number of reagents and various pH values.

4.5 Single Mineral Flotation Test Procedures

Flotation was carried out in a columnar flotation tube with a 40 mm rim diameter, and a height of 200 mm. Conditioning the solutions for flotation was carried out in the exact same manner used in carrying out the settling tests. In all cases however, 2 g of the mineral of interest was used for each test. The total volume of solution used in the flotation tube was 200 mL and so the concentrations of the reagents used were adjusted accordingly, i.e., 50 ppm of starch in a 200 mL solution would account for 10 mL of the total volume.

Before transferring the conditioned contents of the beaker to the flotation cell, the flotation tube was pressurized to avoid solution from seeping through the bottom glass frit. Pressurization of the cell was carried out by briefly turning on the nitrogen cylinder valve attached to the cell through a tube connected to the bottom of it. Once the cell was pressurized, the contents of the beaker were transferred to the cell and distilled water was used to rinse out any settled solids in the bottom of the beaker into the cell. If necessary, additional distilled water was added to the cell to bring the total solution up to the 200 mL mark. The contents in the cell were then stirred for about three minutes prior to adding a drop of Dowfroth 250. An additional three minutes of conditioning was then allowed prior to turning on the nitrogen gas cylinder valve. It was important to ensure that only enough gas was allowed to enter the cell to produce a stable froth as too much gas would cause excessive overflowing of the produced froth and thus inaccurate results.

Upon producing a stable froth, the topmost layer of the froth was collected for either a given time period, or for collecting a specified volume of froth. The froth was collected into a 250 mL beaker. Once the test was complete the nitrogen gas cylinder valve was shutoff along with the magnetic stirrer. The beaker containing the collected froth was first weighed then filtered so that only the solids remained on the filter paper. The filter paper containing the collected solids was then placed in a furnace where it was dried for about an hour. The same procedure was carried out for the tailings in the cell, where the entire flotation cell was also first weighed prior to filtration. In many cases throughout the single mineral flotation tests, three 250 mL beakers were prepared to collect certain amounts of froth. For example, the first beaker was used to collect 25 mL of froth, the second 50 mL, and the third 75 mL of froth product. The contents of each beaker were then separately filtered and dried and the results calculated based on the cumulative amount of solids collected (i.e., solids at 25 mL, 75 mL, and 150 mL). This procedure not only made it possible to carry out fewer tests for each condition but also simplified for each test. Knowing the weights of the empty beaker(s) and flotation cell along with the empty filter papers used in each test, calculations were then carried out to determine the percentage of solids and water recovered with the froth. The percentage of solids recovered was based on the total solids in the froth and tailing as opposed to the total weighed out prior to carrying out each test. This procedure was necessary since some solids were lost during the tests.

4.6 Two Mineral Flotation Test Procedures

Two mineral flotation tests were carried out using the same procedures as single mineral flotation tests with only a number of minor discrepancies.

Two grams of each solid was first weighed out and placed in a beaker containing about 150 mL of distilled water. Conditioning for the two mineral flotation system varied somewhat than for the single mineral flotation tests. The reason for this discrepancy was that the objective in the two mineral flotation tests was to float one mineral (rendered hydrophobic) while at the same time minimize the entrainment and flotation of the other mineral (rendered hydrophilic). For example, in the quartz/hematite and quartz/hydroxylapatite flotation systems, the objective was to float as much quartz as possible while minimize the entrainment of hematite and hydroxylapatite, respectively.

The first procedure in conditioning the two minerals was to add the minerals to the beaker containing 150 mL of distilled water and to then stir the contents prior to adjusting the pH to a desired value. A dispersant (mainly at a concentration of 50 ppm) was then added to the beaker to create an even dispersion of the two minerals and prevent their hetero-coagulation which would be detrimental to the separation process. Conditioning with the dispersant would then be carried out for 3 minutes prior to adding 50 ppm of a depressant (e.g., corn starch). After conditioning with the depressant for an additional three minutes, dodecylamine acetate collector (DDA) was then added (to make a concentration of 1x10^{-4} mol/L) and conditioning would then be carried out for a further three minutes prior to transferring the contents to the flotation cell. Much like with the single mineral flotation tests, it was important to maintain the pH at the desired value. Therefore, if adding one reagent caused the pH to change drastically, the pH would have to be adjusted back to the desired value before adding the next reagent and/or before transferring the solution to the flotation cell.

Since the DDA collector had a tendency to foam easily, particularly in the presence of a gas in solution, it was determined that there was no real need to add any frother. As a result most two mineral flotation tests were carried out using no frothers.

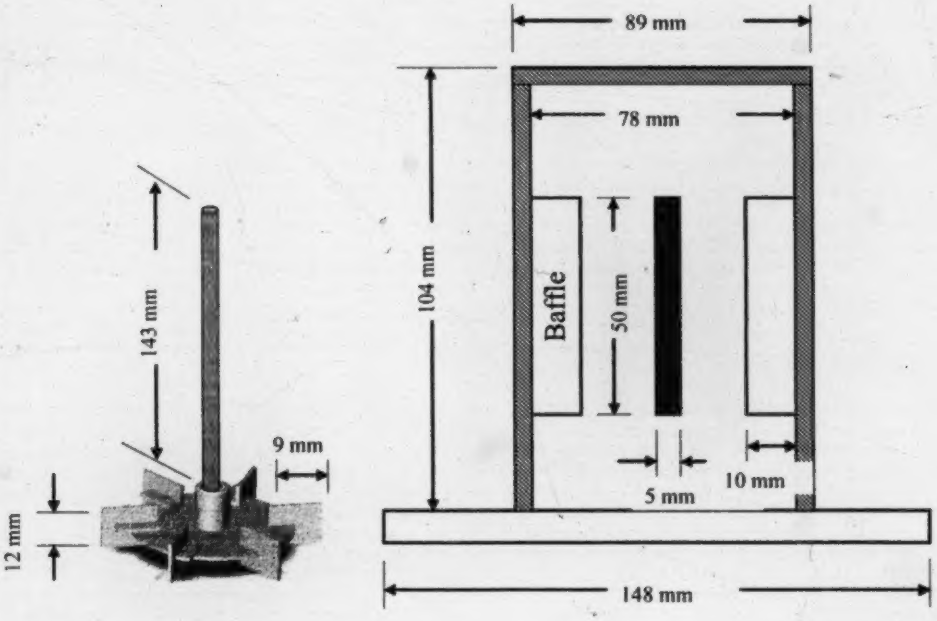
Analyzing the froth and tailing products was a crucial procedure which varied from one particular two mineral system to the next. For the hematite/coarse quartz system, a sieve with the proper mesh size was chosen to allow only hematite to pass through. In this case a large amount of water was required to wash the particles several times in order to ensure that all of the hematite particles had passed through the mesh while all the coarse quartz particles remained on it. The two separated minerals were then filtered, dried and weighed. Since both the froth and tailing products had to be washed with water several times to ensure proper separation of the minerals, the entire procedure proved to be quite cumbersome and time consuming making this a disadvantage for the analysis of the hematite/coarse quartz flotation

Using a proper sieve for the hematite/fine quartz system was not possible since both particles were almost similar in size. As a result the froth and tailing products from these tests were shipped out to International Plasma Laboratory in Vancouver, B.C. for analysis.

For the hydroxylapatite/fine quartz and hydroxylapatite/coarse quartz systems, the two minerals in each system were separated based on the knowledge that hydroxylapatite is easily soluble in strong acids. Therefore in order to separate the two minerals present in both the froth and tailing products, both the froth and tailing were separately filtered and dried. Once dried, the weights of the solids were recorded and the solids transferred to a beaker where about 50 mL of 0.1 M nitric acid (HNO_3) was added to the solids. The contents of the beaker were then agitated for 3 min to ensure that enough time was allotted for the hydroxylapatite to dissolve. The remaining quartz solids were then filtered and dried for at least an hour prior to recording the amount of quartz recovered from each of the froth and tailing. By carrying out such a procedure it was then possible to determine how much hydroxylapatite was recovered from the froth.

4.7 Agitation Procedures

As discussed earlier in the literature review, agitation in fine particle flotation is a common practice for forming hydrophobic flocs of the mineral to be floated (quartz in this research). The effects of agitation on assisting the formation of hydrophobic flocs or even possibly breaking the hydrophilic flocs in two mineral flotation tests were examined. Agitation was carried out using an Arrow 1750 agitator. This agitator contained a dial that was used to adjust the speed of agitation. After conditioning the solution and prior to transferring it to the flotation cell, the solution was placed in the agitation cell of the agitator and agitated for a certain period of time and for various speeds. Flotation on that solution was then carried out and the results were compared to the results of the flotation tests where no agitation was used. As will be seen in the results of this research, the difference in results between the tests where agitation was used to those were no agitation was used was minimal, and therefore agitation was not used very often. This may have also been due to the fact that the DDA collector was observed to have a powerful flocculation effect on quartz particles, specifically at pH~10. Figure 4 illustrates the Rushton impeller (Impellers, www.postmixing.com, 2005) and a vertical cross-sectional view of the agitation cell used for the agitation procedures. Three of the four baffles present in the agitation cell can be seen in the cross-sectional view of the agitation cell. Dimensions of both parts can be seen from the figure.


89 mm
78 mm
104 mm
Baffle
50 mm
143 mm
9 mm
12 mm
5 mm
10 mm
148 mm

Diagrams are Not to Scale

Figure 4: Schematic Illustration of the Rushton Impeller (Impellers, www.postmixing.com, 2005) and a Vertical Cross-Sectional View of the Plaxiglas Agitation Cell used in the Agitation Procedures

4.8 Particle Size Analysis Procedures

In this research, particle size analysis was used to determine the particle sizes of the minerals used when no reagents were added, as well as to quantitatively verify the suspected observed effects that various reagents had on the flocculation of minerals during flotation. For example, the purpose of a polymer depressant is to form flocs of the hydrophilic particles of a mineral which resist entrainment due to their larger size. These flocs are larger than the individual particles that make up each floc and so particle size analysis should not only verify this increase in size, but also provide a quantitative value of the size increase.

Particle size analysis was carried out using a Malvern Instruments Mastersizer 2000. Both hematite and hydroxylapatite minerals were used in these tests. Quartz, however, was not used due to the fact that it had a tendency to badly contaminate the machine.

The first step in carrying out particle size analysis was to take about two grams of the mineral to be tested and to place the sample in a flask containing deionized water. The flask was then sealed and placed in the Aquasonic model 150 HT ultrasonic bath for 5 min to ensure that all the particles were well dispersed prior to the addition of any reagents. The solution containing the sample was then transferred to a beaker for conditioning in the same way that samples were conditioned before performing the settling and flotation tests. Once conditioning was complete, the sample was subjected to size analysis.

The first step in using the machine was to look up the refractive index values for the materials to be examined. The software was then loaded and the values entered into a file containing the mineral names. Procedures for carrying out the particle analysis tests were carried out by simply following the step by step instructions in the software program itself. Very little sample was required for each test and the sample was added to the machine's compartment using a pipette so that it would be easy to control the amount of drops added.

It should be noted that due to the requirements of the Malvern Mastersizer, only deionized water was used, and therefore, only deionized water was added to the minerals, as well as for preparing the reagents used such as sodium metaphosphate and starch.

4.9 Zeta Potential Analysis

The main purpose for carrying out zeta potential measurements was to examine the effects of various pH values on the extent to which identical mineral particles would repel or attract one another using various reagents. The results in return would provide a better understanding of the occurrences observed in the flotation tests.

The zeta potential measurements were performed in the ZetaPals zeta potential analyzer manufactured by Brookhaven Instruments Corporation. All solutions and reagents were prepared in stock solutions of 10^{-2} mol/L KCl in 1 L volumetric flasks. One gram of the mineral to be tested was added to a flask containing one of the KCl solutions. The sealed flask was then shaken a couple of times and inverted to keep the mineral well dispersed in the solution. The additional solutions that were prepared in the KCl solutions included the acid and base modifiers (0.1 M NaOH and 0.1 M HNO_3), and the reagents that were used such as the dispersants and depressants.

Using the solutions prepared, the next step was to condition the samples prior to carrying out the zeta potential tests. Since it is a requirement of the ZetaPals instrument that very little sample be used, 10 mL of the solution containing the mineral of interest was siphoned out of its corresponding stock solution diluted by a factor of ten. In other words the total amount of conditioned solution prior to carrying out the zeta potential analysis was 100 mL. This amount included the 10 mL from the mineral stock solution and the reagents used. A very small amount of this conditioned solution was placed in a plastic cell. An electrode was then immersed into the cell and the combined structure was connected to a phone jack-like connector located in a compartment in the ZetaPALS instrument. After preparing the files for the samples and entering information on the computer system of the analyzer, measurements of the zeta potential began. The machine would perform analysis on each sample ten times and calculate the average value. If some of the results deviated much from the majority, they were manually deleted. The same procedure was repeated for various reagents at various pH values. It was important to dispose of the cells whenever a new reagent was used to avoid cross-contamination.

5 RESULTS AND DISCUSSION

5.1 Single Mineral Settling and Flotation Behavior

5.1.1 *Hematite (Fe_2O_3)*

The settling behavior of the single mineral hematite (Fe_2O_3) with the use of various reagents and pH conditions is presented in Figure 5. To account for the fact that in all the tests some solids were already present in the bottom 50 mL of the 250 mL pulp, the "degree of flocculation" was determined as the total percentage of solids that were settled minus 20%. This 20 % would represent the approximate amount of solids that were present in the bottom 50 mL prior to the start of each test. For each test, 5 g of hematite solids were used and the reagent concentrations were 50 ppm (mg/L). Settling was carried out for 2 minutes. As can be seen from this figure, when corn starch was used nearly all of the hematite settled. At pH 2, a significant amount of solids settled but to a lesser degree than that at the higher pH values. When carboxymethyl cellulose (CMC) of molecular weight 700,000 was used, the majority of the hematite particles were settled at pH values between 2 and 10. At pH 12, however, a significant decrease in the amount of settled solids was observed. By observing the curve representing sodium metaphosphate, it can be seen that across almost the entire pH range, very little solids (less than 20%) settled. Finally by using the CMC with a molecular weight of 80,000, it can be seen that the results obtained were quite diverse. At pH 2 the settling behavior of hematite using this CMC was very similar to that obtained with the higher molecular weight CMC. However, at higher pH values, the amount of hematite solids settled decreased drastically and at pH 12 the settling behavior was very similar to that obtained when using the dispersant sodium metaphosphate.

These results indicate that for the hematite mineral, starch and CMC with a molecular weight of 700,000 are good flocculants over a broad pH range. The results obtained with the lower molecular weight CMC (M.W = 80,000) indicate that this reagent can behave as both a depressant and dispersant depending on pH. Based on the results of Figure 5, this lower molecular weight CMC behaves more as a flocculant at lower pH values and more as a dispersant at high pH values. The results obtained with sodium metaphosphate clearly indicate that sodium metaphosphate is a strong dispersant as expected since very little solids were settled over the entire pH range studied.

As mentioned earlier, the purpose for carrying out the settling tests was to examine the degree to which particles would flocculate or disperse when using a combination of various reagents and conditions (pH). If particles are well flocculated and as a result settle quicker, then it should be expected that during flotation their entrainment would be lower.

Figure 6 illustrates the hematite flotation results obtained using the same reagents that were used for the settling tests. The results for the tests carried out at pH values close to 7 are reported here since the lowest recoveries of hematite were observed when using corn starch at this pH. No collector was used for this set of tests, so that the genuine flotation of the hematite in the froth product would be zero, and any amount that was recovered would be due to mechanical entrainment. The dotted diagonal line in the graph represents entrainment behavior in which solid recovery equals water recovery. Any curves that lie below this line would indicate low entrainment, while any curve close to or on this line would indicate strong entrainment. Curves that lie above the entrainment line represent genuine flotation. As can be seen from Figure 6, corn starch usage resulted in almost no entrainment of the hematite. The higher molecular weight CMC (M.W = 700,000) also produced very similar results to corn starch; however, slightly more solids were entrained. On the contrary, however, the lower molecular weight CMC (M.W= 80,000) showed significant entrainment since more solid particles were recovered and since the curve representing this reagent is closer to the entrainment line. It is interesting to note that the curve representing sodium metaphosphate is within very close proximity to the entrainment curve indicating that sodium metaphosphate is a very powerful dispersant and that using sodium metaphosphate causes high entrainment of the hematite particles.

The results of Figure 6 are in agreement with the results discussed in Figure 5 in that the reagents that allowed flocculation and fast settling of the hematite particles were the same reagents that minimized entrainment. On the other hand, the reagents that caused the particles to settle slowly were the same reagents that allowed the most entrainment.

5.1.2 Hydroxylapatite ($Ca_5(OH)(PO_4)_3$)

In order to study the flotation behavior of hydroxylapatite (also known as calcium phosphate), settling tests were also carried out so that the flocculation patterns of this mineral could first be observed. All the settling tests with this mineral were carried out at a pH value of 10. Preliminary trial and error tests indicated that these settling tests be carried out for 5 min as opposed to only 2 min like that used for hematite. Perhaps this difference in time was due to the fact that the hydroxylapatite particles were more finely dispersed and also lighter than the hematite particles. Figure 7 presents the flocculation and settling behavior for hydroxylapatite with the use of various reagents. The results displayed on this figure are very similar to those obtained for hematite with the exception of the behavior of the corn starch and higher molecular weight CMC. In this set of results it appears as though the higher molecular weight CMC allowed better flocculation and thus settling of the hydroxylapatite than corn starch. Sodium silicate and sodium metaphosphate, both of which are dispersants, produced similar settling results for hydroxylapatite as did the lower molecular weight CMC.

It is worth mentioning that perhaps the reason why slightly more solids appeared to have settled when no reagents were being used than when dispersants such as sodium metaphosphate or sodium silicate were used is that, contrary to initial thoughts, there may have been small flocs of the mineral present in the bulk hydroxylapatite material. The addition of dispersants to this material may have broken up such flocs thus reducing their settling rate. Visually, however, the hydroxylapatite powder did appear well dispersed prior to carrying out any tests.

Figure 8 illustrates the flotation results obtained for hydroxylapatite using various reagents. All tests were carried out at a pH of about 10 and 2 g of the mineral was used for each test. No collector was used; however, DF 250 frother was used to produce and maintain a steady froth. The curves representing the higher molecular weight CMC and corn starch deviate significantly below the entrainment curve indicating low entrainment, whereas the curve representing sodium metaphosphate overlaps with the entrainment curve indicating very high entrainment. Adding no reagent, or using sodium silicate, dextrin, or the lower molecular weight CMC, resulted in curves that only slightly deviate below the entrainment curve which indicates that these reagents had somewhat of a flocculation effect on hydroxylapatite but not to the extent that corn starch or the higher molecular weight CMC did. In addition to this observation, these reagents (sodium silicate, dextrin, and the lower molecular weight CMC) did not disperse the particles to the degree that sodium metaphosphate did and, therefore, did not make them vulnerable to extreme entrainment either. Such an observation also indicates that sodium metaphosphate is a more powerful dispersant compared to sodium silicate. The flotation results are once again in agreement with the corresponding settling tests obtained for hydroxylapatite in that the reagents which caused the most flocculation and settling of the mineral, resulted in the least entrainment during flotation and vice versa.

5.1.3 Sphalerite (ZnS)

Figure 9 illustrates the settling test results obtained for -38 μm sphalerite solid particles. As can be seen from this figure, very little solids were settled in all cases including those where corn starch and zinc sulfate were used. Despite this observation, however, both corn starch and zinc sulfate allowed the most settling to occur.

Figure 10 illustrates the flotation results obtained for the sphalerite mineral. As can be seen from this figure, using corn starch or zinc sulfate appeared to minimize the entrainment of sphalerite. The extent to which they minimized the entrainment of the spahlerite was not too significant, however, considering that both curves representing this reagent lie relatively close to the entrainment line. The curve representing the higher molecular weight CMC appears above the entrainment line and so, unlike the cases of hematite and hydroxylapatite where this reagent was an effective flocculant and depressant, the higher molecular weight CMC did not appear to have much of an effect on the sphalerite particles. The curves representing the lower molecular weight CMC, sodium metaphosphate, and dextrin are also above the entrainment line, with the curve representing the lower molecular weight CMC being the furthest away from this line.

It is interesting to note that despite the fact that no collector was used in the sphalerite flotation tests, all four curves above the entrainment line in Figure 10 exhibit genuine flotation behavior. In other words, sodium metaphosphate, dextrin, and both the higher and lower molecular weight CMC reagents not only failed to effectively depress sphalerite in order to reduce its entrainment, but also failed to depress the genuine flotation of the sphalerite. On the other hand both corn starch and zinc sulfate have managed to depress the genuine flotation and entrainment of sphalerite. The depressing effect of both these minerals, however, was not too powerful as mentioned. One strong possibility for the observed results of Figure 10 is that the sphalerite mineral was slightly oxidized and thus became floatable.

5.1.4 Galena (PbS)

Due to the fact that very little galena solids were present in the laboratory, no settling tests were carried out with this mineral. However enough material was present to perform flotation tests and Figure 11 illustrates these results. Two grams of galena were used for each test.

From the results in Figure 11 it can be seen that corn starch and the higher molecular weight CMC were the most effective reagents for minimizing the entrainment of the galena since both curves representing these reagents lie significantly below the entrainment line. The curve representing dextrin lies only slightly below the entrainment line, and so this could indicate that dextrin may have slightly flocculated the galena particles but not to the extent of significantly minimizing its entrainment. The curves representing sodium metaphosphate, potassium dichromate, and the lower molecular weight CMC, all lie above the entrainment line which indicates genuine flotation behavior.

When comparing the results of both sulphide minerals together, it can be seen that the higher molecular weight CMC performed much better for galena than it did for sphalerite despite the fact that galena was most likely oxidized as well. Corn starch also performed slightly better with galena than with sphalerite. The difference, however, was not too significant. Sodium metaphosphate displayed genuine flotation behavior for both minerals. It is uncertain as to why potassium dichromate, a typically used depressant for galena, displayed such powerful genuine flotation behavior for the mineral considering that corn starch and the higher molecular weight CMC not only depressed the genuine flotation behavior of the same galena mineral but also minimized its entrainment. It may well be that in order to effectively adsorb onto the surfaces of the galena particles, potassium dichromate requires that the particles be non-oxidized.

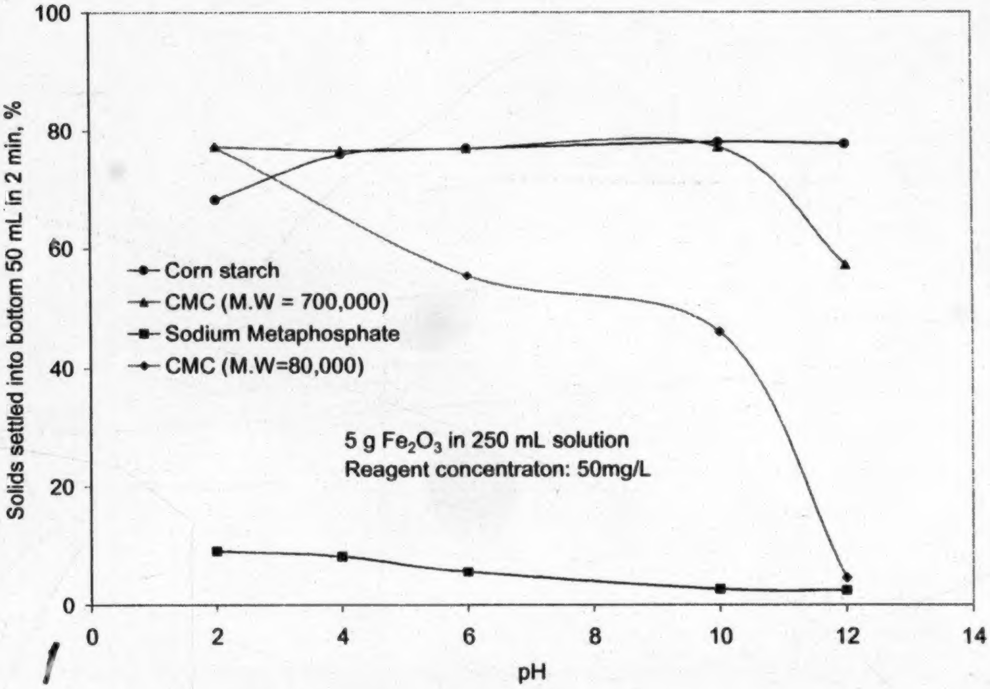


Figure 5: Hematite Flocculation and Settling Behavior using Various Reagents as a Function of pH

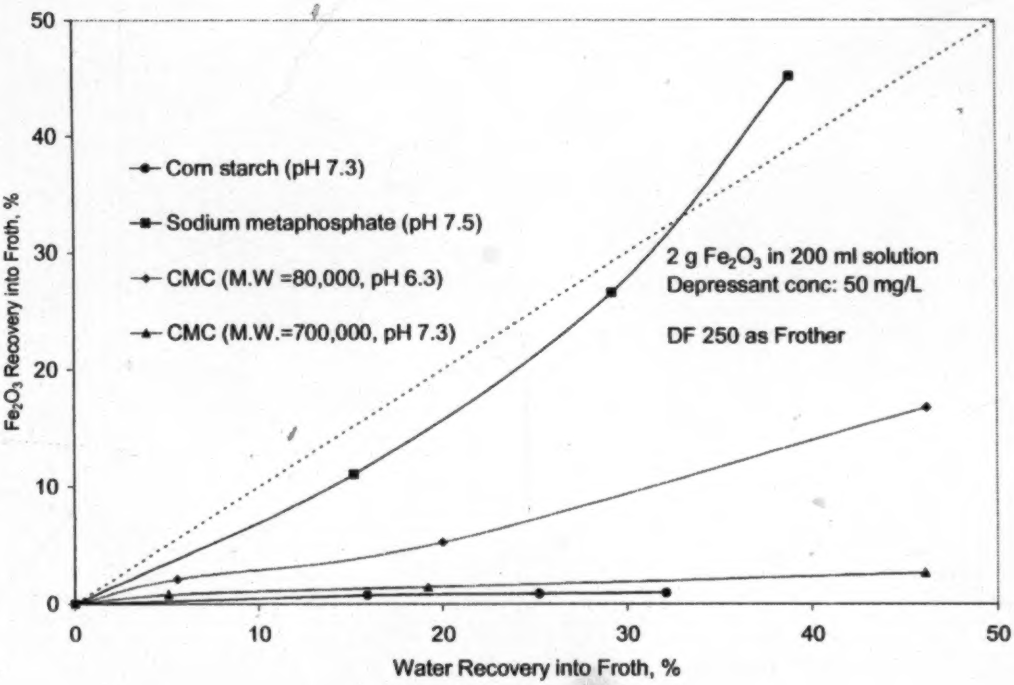


Figure 6: Entrainment Behavior of Hematite into the Froth in the Presence of Various Reagents

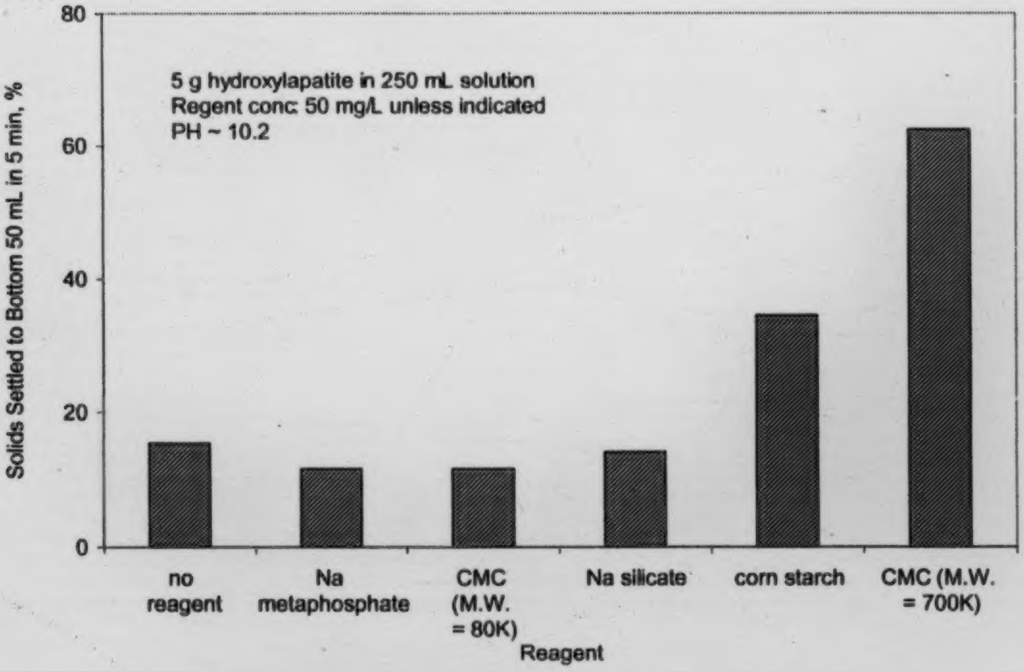


Figure 7: Hydroxylapatite Flocculation and Settling Behavior using Various Reagents

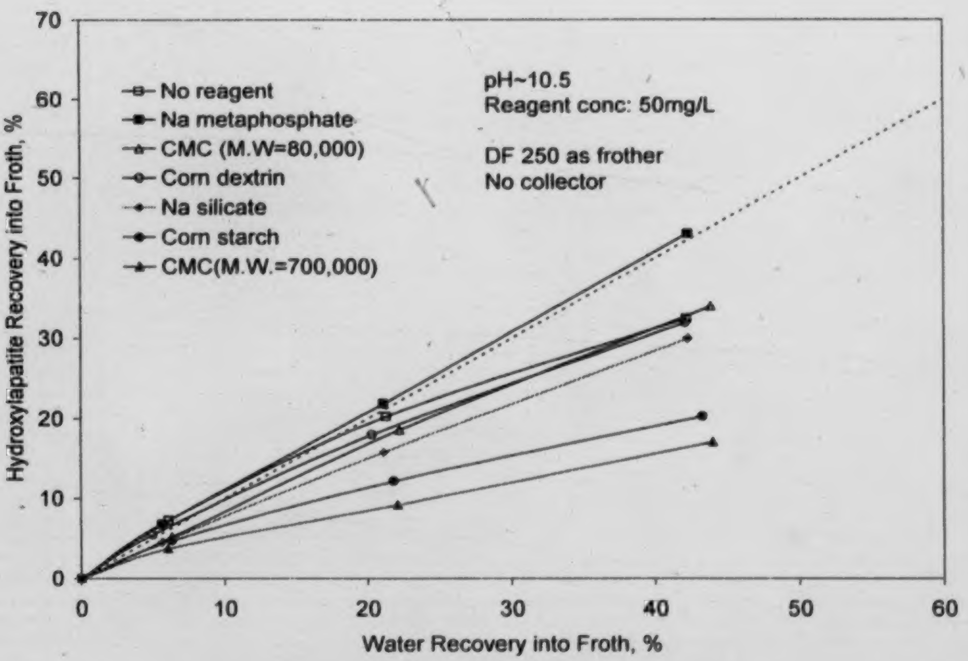


Figure 8: Entrainment Behavior of Hydroxylapatite into the Froth in the Presence of Various Reagents

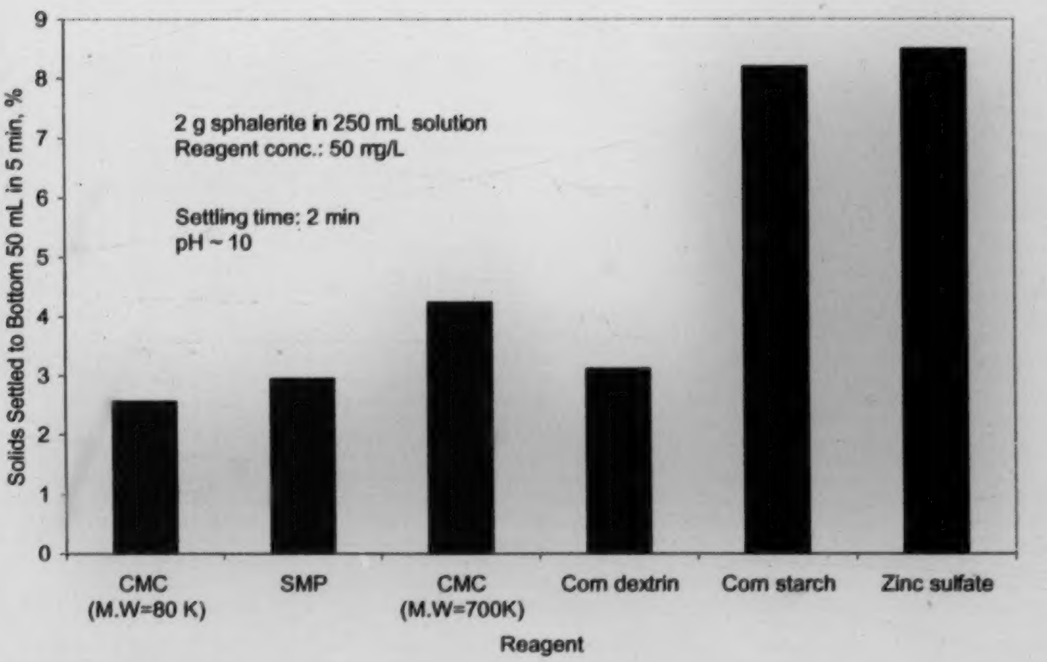


Figure 9: Sphalerite Flocculation and Settling Behavior using Various Reagents

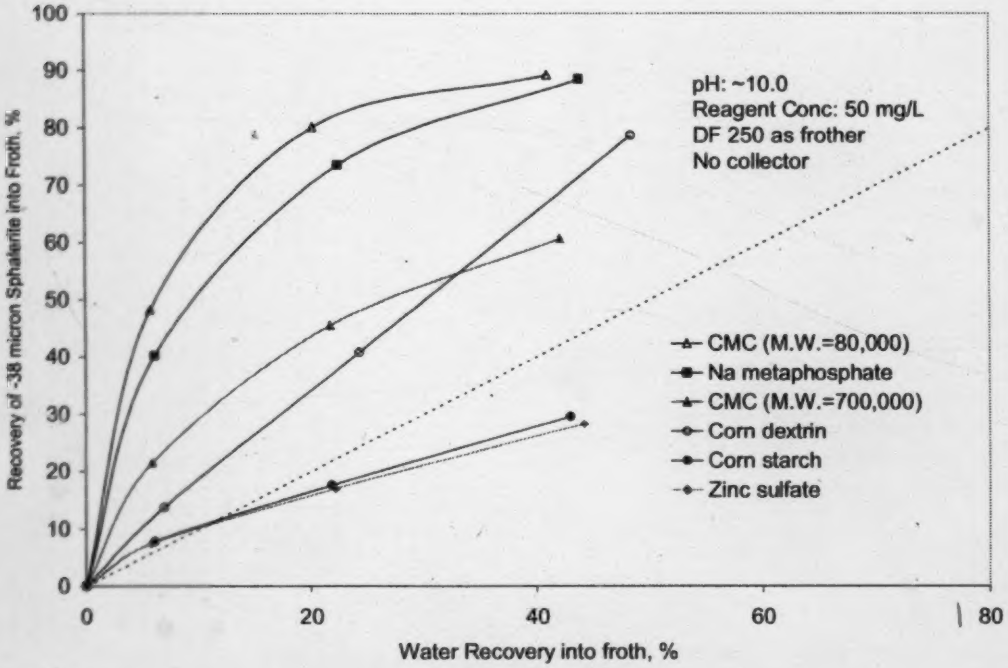


Figure 10: Entrainment Behavior of Sphalerite into the Froth in the Presence of Various Reagents

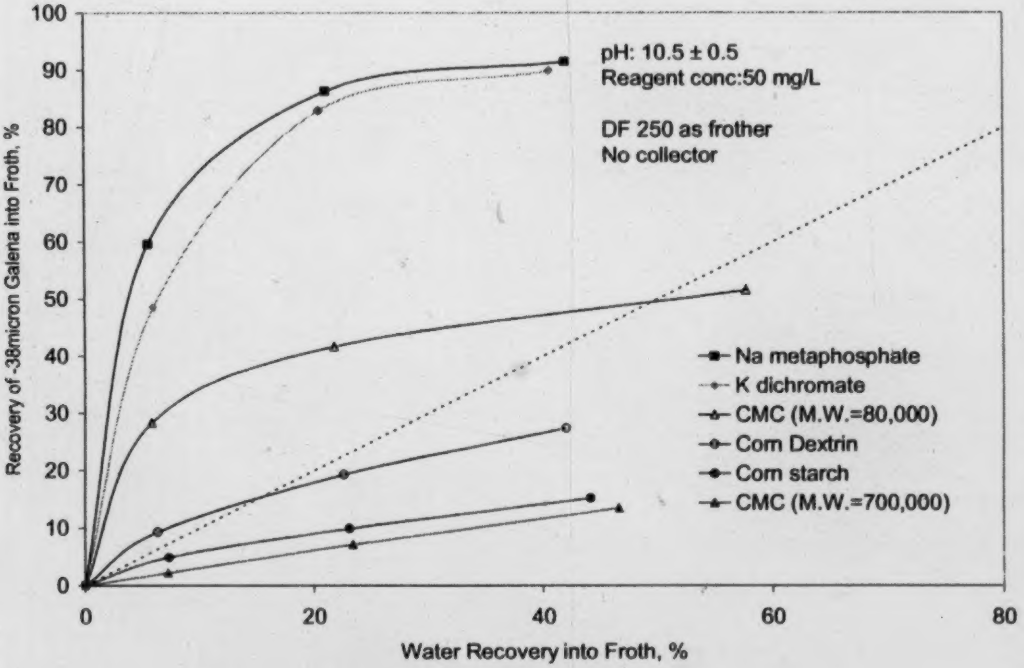


Figure 11: Entrainment Behavior of Galena into the Froth in the Presence of Various Reagents

5.2 Two Mineral Flotation Behavior

5.2.1 Hematite/Coarse Quartz Flotation

The flotation of an equal mixture of hematite and coarse quartz is presented in Figure 12. Flotation time for all the tests was 7 min and although the DDA collector was observed to be effective in forming a froth, it was often found that after a few minutes of flotation, the froth would start to destabilize. It was, therefore, necessary to add a drop of DF 250 frother to reform and stabilize the froth.

A first glance of Figure 12 may not make it immediately clear as to which set of reagents used produced the best results. However, it is important to note that the objective in this set of tests was to try to recover as much quartz as possible while at the same time keep the entrainment of hematite to a minimum. Therefore, it is the separation efficiency that is of interest in the analysis of these results. Separation efficiency (S.E) is defined as the difference between the amount of (hydrophobic) quartz recovered minus the amount of (hydrophilic) hematite recovered.

Table 4 summarizes numerically the separation efficiencies of the results illustrated in Figure 12.

Table 4: Separation Efficiencies of the Cationic Collector Flotation of Coarse Quartz-Iron Oxide Mixtures at pH 10 with Various Reagents

Reagent(s)	**Water Recovery, %**	**Separation Efficiency, %**
Na silicate + corn starch + DDA	5.65	67.4
Sodium metaphosphate (SMP) + DDA	18.5	42.3
Sodium metaphosphate + corn starch + DDA	8.31	66.1
Corn starch + DDA	5.94	83.6
Corn dextrin + DDA	11.2	76.2
CMC (molecular weight = 700,000) + DDA	7.02	11.9
CMC (molecular weight = 80,000) + DDA	21.4	16.8

The first set of bars in Figure 12 represent a typical two mineral flotation system in that typically a dispersant is normally used first, followed by a depressant and finally a collector. Although this result illustrates a significant amount of quartz and a low amount of hematite recovered, the set of bars representing the effect of using corn starch alone did produce better results since the separation efficiency was even higher in this case than in the case where sodium silicate dispersant was added prior to the addition of the corn starch (i.e., the amount of quartz recovered was higher while the amount of hematite recovered was lower). It can also be seen that by using sodium metaphosphate alone, nearly all of the quartz was recovered; however, at the same time, entrainment of hematite was severe. Similar results can be seen with the lower molecular weight CMC. However, the separation efficiency was even lower in this case since less quartz and more hematite was recovered indicating the use of the lower molecular weight CMC was in fact worse than that of sodium metaphosphate. Given that dextrin did not perform well in terms of effectively depressing hematite in the single mineral flotation system, it is interesting to note a relatively high separation efficiency (see Table 4) using this reagent. This observation with dextrin is especially true considering that a relatively lower amount of hematite was recovered using this reagent. On the other hand, the higher molecular weight CMC, previously observed to effectively flocculate hematite in the single mineral flotation system, produced the lowest separation efficiency in this system. Based on the results of Figure 12 and Table 4 alone, corn starch was the most effective reagent since its corresponding separation efficiency was the highest. In making such a conclusion however, it is important to note that although the hematite recovery was the lowest for this case, the quartz recovery was not the highest.

It was mentioned earlier that water recovery alone is insufficient to account for entrainment since the degree of flocculation can also play a role in this. For this reason it cannot be argued that variations in water recovery among the results of Figure 12 account for the differences in the amount of hematite entrained in each test. However, since more research would have to be performed to examine this phenomenon, at this point water recovery should still be taken into consideration when analyzing such results. Figure 13 presents the results of Figure 12 in an alternative format. Here the results are plotted such that the amount of solids recovered for each reagent used is a function of the amount of water recovered. The separation efficiencies are also more clearly observed by plotting the results in such a manner. Each square point in Figure 13 represents the recovery of quartz for a given reagent system, and is labeled with the reagent it represents. Directly below each square point is the corresponding hematite recovery, represented by circle points. Obviously the closer the quartz recovery point is to its corresponding hematite recovery point, the lower the separation efficiency.

A quick glance at the results of Figure 13 illustrates that using corn starch alone produced the best separation efficiency due to the greatest separation distance between the two corresponding legends representing the quartz and hematite recoveries. The use of the sodium silicate dispersant prior to the addition of starch did not perform as well as when starch was used alone. A possible explanation for this behavior may be due to the possibility that the adsorption of the dispersant on the surface of the hematite particles interfered with the adsorption of starch.

Although the water recovery in the case where the higher molecular weight CMC was used was similar to that of corn starch, it was mentioned that this CMC produced poor separation results and in fact the lowest separation efficiency. This is probably due to the fact that at this pH, CMC caused the hematite particles to become negatively charged. Since DDA is a cationic collector, the force of attraction between the negatively charged hematite particles and the cationic collector may have been strong enough to cause the hematite particles to be recovered into the froth. Recall also that no collector was used in the single mineral flotation tests of hematite and so the recovery of hematite was low in that case.

The use of sodium metaphosphate prior to the addition of corn starch allowed for a significant amount of separation; however, entrainment was also higher in this case than that where sodium silicate was used prior to the addition of the depressant. This result is expected since it was seen earlier that sodium metaphosphate was a strong dispersant with hematite, making it more difficult for the starch to effectively flocculate the hematite. As can be seen from Figures 12 and 13, the use of sodium metaphosphate alone allowed more quartz to be recovered but at a much lower grade since more hematite particles were also recovered. Such results do indicate the importance of a depressant such as corn starch in separating fine hydrophilic gangue material from the hydrophobic material.

5.2.2 Hematite/Fine Quartz Flotation

The hematite/fine quartz mineral flotation system is a more realistic representation of a flotation system typically encountered in an industrial situation. This is due to the fact that the majority of the minerals involved in the flotation process are more or less the same size, since the minerals in a given system originate from the same crushed ore.

It was discussed earlier that hydrophobic flocculation is an important procedure in fine particle flotation as it ensures that the hydrophobic particles are well flocculated together, which in turn increases the bubble-particle collision probability. To examine the effect that hydrophobic flocculation would have on the recovery of the hydrophobic quartz particles as well as on the possible breakup of hydrophilic flocs, a number of agitation tests were carried out at various speed and time periods. Results from such tests would be beneficial for both the hematite/ fine quartz and hydroxylapatite/fine quartz systems.

5.2.2.1 Hydrophobic Flocculation (Agitation Tests)

A number of flotation tests were conducted on the fine quartz particles (-20 μm) after agitating these particles for various time periods and speeds (Figures 14-16). In each test 2 g of the fine quartz particles were used and agitation tests were carried out at 300, 600 and 1100 rpm at agitation time periods of 5, 15 and 20 min. Conditioning of the samples prior to agitation was carried out at pH 10. Upon completion of these various agitation tests, flotation tests were conducted. Each flotation test was carried out for a duration of 7 min. Note that on each of the three figures (Figures 14-16) there are two pairs of water and corresponding solid recovery curves. The difference between these two types of curves was the use of a drop of frother which produced the set of results represented by the cumulative recovery curves. Initially, it was observed that in these tests the froth produced by the addition of the DDA collector would start to destabilize after only 4 min of flotation and so for the remaining 3 min, a drop of DF 250 frother had to be added to reform and stabilize the froth. However, the froth formed by the addition of this frother was found to produce very fine bubbles (which is known to increase entrainment). Therefore, in order to obtain more accurate results, the froth product formed during the first 4 minutes was collected in a separate beaker than that formed during the remaining 3 min and the two curves were plotted separately. In discussing the results, reference will be made to the curves representing the flotation tests where no frother was added since these flotation results are more genuine.

Figure 14 presents the flotation results obtained by first agitating the quartz particles for 5 min at various agitation speeds prior to flotation. By observing the solid and corresponding water recovery curves, it can be seen that for the most part, the amount of solids recovered was constant regardless of the agitation speed used. However, in the absence of agitation, almost all the quartz particles were recovered after 7 min of flotation. The amount of quartz recovered however, dropped slightly after using agitation. Such an observation implies that the quartz particles were probably flocculated through the addition of the DDA collector and that the agitation probably broke up the flocs to some degree. This observation also indicates the sensitivity of the flocs to agitation considering the particles were agitated for only 5 min.

Figure 15 illustrates the flotation results of the quartz particles agitated for 15 minutes prior to flotation. For the most part the results are similar to those obtained for the 5 minute agitation tests (Figure 14). The only observed difference occurred at 300 rpm where froth recovery was lower than that obtained for the 5 minute agitation time period at this speed. This observation was based on the non cumulative recovery curves. The cumulative recovery curves display more or less the same behavior as observed in the 5 minute agitation flotation results. The fact that the results between the 5 min and 15 min agitation results were similar may well indicate that a 10 minute increase is unlikely too significant in affecting the formation or breakup of the quartz flocs.

Figure 16 presents the flotation results of the quartz particles agitated for 20 minutes prior to flotation. As can be seen from this figure, it is here where actual observable differences between the agitation time periods can be seen. With reference to Figures 14 and 15 it can be seen that from Figure 16 at 300 rpm, the recovery of the quartz particles fell slightly, while at 600 rpm the recovery of the quartz particles increased by about 10% compared to that at 300 rpm. The real major difference was observed at the agitation speed of 1100 rpm where the amount of quartz recovered dropped drastically to about 30%. The results displayed in Figure 16 are interesting since they show what typically is expected in agitation. That is to say at too low an agitation speed, flocs may break and then reform at higher agitation speeds. However once the agitation speed exceeds a specific value, most of the flocs are broken up permanently leading to a low recovery of the hydrophobic particles.

Overall in all three cases the use of shear in assisting hydrophobic flocculation did not appear to fulfill the desired purpose for which it was intended. In fact as discussed earlier and as can be seen from all three figures, the point representing the absence of agitation was the point where almost all the quartz particles were recovered. The reason for this observed phenomenon may well be due to the possibility that the DDA collector possesses flocculating capabilities.

To examine the possible flocculating power that DDA possesses for the fine quartz particles, a number of settling tests were conducted at various pH values using 5 g of the quartz solids. Trial and error tests determined the appropriate settling period to be 2 min for each test. Prior to the settling tests, the quartz particles were conditioned with 10^{-4} mol/L of DDA at various pH values. Although it was mentioned that settling tests in this research were conducted in 250 mL graduated cylinders, to eliminate the formation of froth from the DDA during the shaking and inversion procedure, the entire cylinder was filled with distilled water so that there would be no air present above the liquid surface which would assist in froth formation. This extra amount of water was found to be 20 mL which brought the total amount of water in the cylinder to 270 mL. The total amount of DDA added was adjusted accordingly.

Figure 17 illustrates the settling test results that were conducted on the fine quartz particles to determine what degree, if any, the addition of DDA collector has on flocculating quartz. As can be seen from this figure, 95% of the quartz particles were settled after the 2 min settling test at pH 10. Only about 20% of the solids were settled at the remaining tested pH values. The results of Figure 17 definitely indicate that the quartz particles were well flocculated by DDA at pH 10. Furthermore the results illustrate that not only was shear unnecessary to help form hydrophobic flocs out of the quartz particles, but that it in fact assisted in breaking up the flocs to some degree thus lowering the quartz recovery.

In order to verify that at pH 10 the DDA collector alone was responsible for flocculating the quartz particles and that various DDA concentrations influence the flocculation of quartz particles, three settling tests on the quartz particles were conducted. The first test involved using no DDA collector, while the second and third tests involved using DDA at concentrations of 10^{-4} mol/L and $5x10^{-4}$ mol/L, respectively. The results of these tests are illustrated in Figure 18. As can be seen from this figure, less than 50% of the quartz solids were settled when no DDA was used compared to almost 100% of settled solids with DDA. Since the two settling tests using DDA were similar regardless of the concentration used, it was found that using a DDA concentration higher than 10^{-4} mol/L would be unnecessary.

The results thus far have indicated that the DDA cationic collector possesses flocculating power for the fine quartz used in this research and that the use of shear to flocculate these quartz particles in the presence of DDA was not necessary. However, complete analysis of the effects of agitation on the breakup or formation of flocs is not complete until the effects of agitation on the hydrophilic hematite flocs are examined as well. Figure 19 presents the flotation results of hematite particles that were first conditioned with corn starch at pH 10 prior to agitation at various speeds. No DDA collector was used; however a drop of DF 250 was used as the frother. As can be seen from Figure 19, entrainment overall was low for the four agitation speeds examined (i.e., 150, 300, 600 and 1100 rpm). At 1100 rpm slightly more solids were recovered; however, there was also slightly more water recovered which may have played a role in this behavior.

5.2.2.2 Settling Behavior of Hematite/Fine Quartz

In order to obtain a general idea as to what was to be expected in the flotation tests, settling tests were carried out involving an equal mixture of both hematite and fine quartz particles together. Dodecylamine acetate (DDA) collector was used in all these tests at a concentration of 10^{-4} mol/L and each settling test was carried out for 3 min based on trial and error findings. Once again to avoid the formation of froth from the DDA added, the entire graduated cylinder was filled with solution (i.e., 270 mL). The purpose of performing settling tests using both minerals was to obtain valuable information regarding how certain reagents affect not only the flocculation of hematite, but also that of quartz in the presence of the DDA collector.

Figure 20 presents the settling (flocculation) test results obtained for an equal mixture of fine quartz and hematite (2.5 g each) under the influence of various reagents. DDA collector at a concentration of 10^{-4} mol/L was used in all tests. The first pair of bars in Figure 20 represents the use of sodium silicate dispersant. It can be seen that by using this dispersant alone, the majority of both solids were settled. The addition of starch after sodium silicate, however, caused much less quartz particles but slightly more hematite particles to settle. Using sodium metaphosphate alone allowed for poor flocculation and settling of both minerals as less than 20% of both solids were settled. Adding starch after sodium metaphosphate allowed more hematite particles to settle; however, there was no improvement for quartz. Finally by using starch alone, it can be seen that a fair amount of hematite was settled while only about 40% of quartz was settled.

A number of theories can be used to explain the results of Figure 20. As seen in the previous section, DDA collector functioned as an excellent flocculant for quartz at pH 10. It is the DDA that was responsible for the settling of quartz in Figure 20. Considering that sodium silicate was not found to be a powerful dispersant, it may well be that by using this dispersant alone, some of the hematite particles were entrapped into the hydrophobic flocs resulting in the high amount of settled hematite particles that was observed. The results obtained when using starch both alone and after the addition of sodium silicate were very similar for the most part. In saying this, however, slightly more hematite solids settled when sodium silicate was added first which was probably due to the fact that the presence of the sodium silicate dispersant allowed for the better selectivity of starch.

The poor settling behavior obtained for the tests involving sodium metaphosphate were expected considering the powerful dispersant effect of this reagent. This can be explained by the fact that powerful dispersants can often make it difficult for a depressant to effectively flocculate minerals, particularly when the depressant is used at a fixed concentration. Compared to the case where sodium metaphosphate was used alone, adding corn starch after sodium metaphosphate produced slightly better results since more hematite particles were settled (Figure 20); however, the amount of hematite settled was only about 30% compared to the 90% settled when sodium silicate was used prior to starch. Therefore, the results seem to indicate that hematite dispersed by sodium metaphosphate cannot be re-flocculated by starch. Based on the results of Figure 20, the best results were probably obtained when using sodium silicate prior to starch.

5.2.2.3 Flotation Behavior of Hematite/Fine Quartz

The flotation tests carried out on the hematite and fine quartz (-20 μm) are illustrated in Figure 21. Table 5 numerically summarizes the separation efficiencies of the results illustrated in Figure 21.

Table 5: Separation Efficiencies of Cationic Collector Flotation of Fine Quartz-Iron Oxide Mixtures at pH 10 with Various Reagents

Reagent	Water Recovery, %	Separation Efficiency, %
Na silicate + starch + DDA	11.9	62.8
Na metaphosphate + DDA	20.1	35.3
Na metaphosphate + starch + DDA	17.1	10.2
Starch + DDA	24.1	3.90
Starch + DDA (no frother)	16.4	45.5

Recall that the objective for conducting the set of flotation tests involving an equal mixture of fine quartz and hematite was to float as much quartz as possible while keeping the entrainment of hematite to a minimum. Since it was often difficult to keep a steady froth by simply using DDA alone, a drop of frother was added after the first 4 minutes of flotation (total flotation time was 7 min). This was consistent for each test and, although the frother may have permitted more than unusual recovery and entrainment, nevertheless relative comparisons between the tests were still possible. Although it was mentioned earlier that agitation in this research was unnecessary, agitation was still carried out in these set of tests to be consistent with the fact that hydrophobic flocculation is typically used in flotation. In addition to this reason, a moderate degree of agitation is beneficial to dispersion.

The first set of bars in Figure 21 represents the recovery of both the fine quartz and hematite when using sodium silicate followed by starch. From this set of bars, it can be seen that the separation efficiency is reasonable considering that a large amount of quartz and much less an amount of hematite were recovered. When sodium metaphosphate was used alone it can be seen that along with a slightly higher water recovery, the separation efficiency was lower in that a significantly lower amount of quartz and a slightly higher amount of hematite were recovered in comparison to the first set of bars where sodium silicate and starch were used. Interestingly enough and contrary to what would normally be expected, more hematite was actually recovered in the case where corn starch was used with sodium metaphosphate than in the case where sodium metaphosphate was used alone (i.e., separation efficiency was lower when starch was added after sodium metaphosphate than when sodium metaphosphate was used alone). When corn starch was used alone, both the quartz and hematite percent recoveries were high and similar to each other, resulting in an extremely low separation efficiency. However it should be noted that the water recovery was also somewhat higher for this case which may have played a role in this result. The last set of bars in Figure 21 represents the use of corn starch with no frother being used. This test was carried out simply to determine how much of a difference the addition of a frother would make. From this set of tests it can be seen that with no frother added, much less mechanical entrainment of hematite was obtained compared to the case where corn starch was used with a frother. In saying this, however, it is important to note that much less quartz was also recovered.

The results of Figure 21 for the fine quartz/hematite flotation are in general considered fairly poor. For example, in all cases the entrainment of hematite was over 20% which is considered high. The most interesting and unexpected result was obtained with corn starch in the presence of a frother, but in the absence of sodium silicate dispersant. As mentioned above, although a high amount of quartz was recovered in this case, hematite entrainment was the most severe. The most logical explanation for such a result would be that the absence of a dispersant allowed no selectivity of the starch to occur. This theory is most likely to hold true considering that when sodium silicate was used prior to starch, the separation efficiency was much higher with hematite entrainment being significantly lower. Although it was noted that the water recovery for the case where starch was used alone was the highest, it was not enough to justify the severe entrainment observed. The results do indeed point out the crucial need for a suitable dispersant prior to the addition of a depressant in flotation. Without a dispersant, less depressant is available for the target mineral as some of the starch would also adsorb on the surfaces of other minerals in a flotation pulp. Hetero-coagulation also definitely plays a role in the absence of a dispersant since entrapment of the hydrophilic particles into the hydrophobic flocs or vice versa is possible.

The fact that at similar water recoveries, more hematite was recovered after the addition of starch to sodium metaphosphate than in the case where sodium metaphosphate was used alone, is also contrary to logic expectations. In fact earlier it was observed in Figure 20 that the addition of starch after sodium metaphosphate actually flocculated slightly more hematite and so it is uncertain as to why more hematite was recovered after the addition of starch during flotation. More research into the effects of sodium metaphosphate as a dispersant in flotation would have to be conducted.

Using a frother allowed more entrainment to occur due to the production of fine bubbles and so it is most likely that the last set of bars illustrated in Figure 21 where no frother was used, is a more accurate depiction of the effects of corn starch for this system. Although less quartz was recovered in the absence of the frother, much less entrainment of hematite also occurred and so there exists a compromise between the recoveries of both minerals in this flotation system.

5.2.3 Hydroxylapatite/Coarse Quartz Flotation

As an alternative to hematite, flotation tests were also carried out on an equal mixture of hydroxylapatite and coarse quartz. The procedures used in each test were identical to the hematite/coarse quartz system; however calcium nitrate at a concentration of 10^{-5} mol/L was used in some of the tests in this section. The results of these flotation tests are illustrated in Figure 22.

To summarize the results observed in Figure 22, Table 6 presents the water recoveries and separation efficiencies (S.E) of all the tests discussed in this section. DDA collector was used and was added last in all these tests.

Table 6: Separation Efficiencies of Cationic Collector Flotation of Coarse Quartz- Hydroxylapatite Mixtures at pH 10 with Various Reagents

Reagent	Water Recovery,%	S.E, %
None	17.8	60.1
Na silicate	14.8	68.0
Na silicate + dextrin	13.8	63.6
Na silicate + starch	15.7	78.9
Na silicate + starch + agitation	14.5	68.7
Ca nitrate + starch	11.8	85.1
Na silicate + Ca nitrate + starch	11.2	85.2
Ca nitrate + Na silicate + starch	11.3	85.1
Na silicate + Ca nitrate (1E-4) + starch	9.93	82.8

With no reagent added, more than 85% of quartz and less than 30% of hydroxylapatite were recovered into the flotation froth resulting in a separation efficiency of about 60%. Very similar results were observed when sodium silicate was used alone. When sodium silicate was used followed by dextrin, the separation efficiency was slightly lower than in the case where sodium silicate was used alone at similar water recoveries. However, when starch was added after sodium silicate, the separation efficiency improved with almost all the quartz being recovered and less than 20% of the hydroxylapatite being recovered. It can be easily seen that in the case where sodium silicate was used followed by starch and then agitation at 1800 rpm for 5 min, at a similar water recovery to the case where sodium silicate and starch with no agitation was used, the amount of quartz recovered dropped slightly while the amount of hydroxylapatite recovered increased slightly resulting in a lower separation efficiency.

The last four sets of bars in Figure 22 represent the flotation results where calcium nitrate was used with starch depressant, either alone or with the sodium silicate dispersant. For comparison purposes, water recoveries were the same for all these tests (~11-12%) with the exception of the last set of bars where the water recovery was approximately 10%. The addition of calcium nitrate prior to starch resulted in an excellent separation efficiency with 98% of the quartz and only 13% of the hydroxylapatite recovered. The use of sodium silicate either before or after the addition of the calcium nitrate did not appear to influence the results very much since the recoveries for both minerals were the same. Using a higher amount of calcium nitrate (10^{-4} mol/L) after the addition of sodium silicate but before the addition of the starch did not appear to have any influence on the amount of quartz recovered; however, slightly more hydroxylapatite was entrained in this case when comparing it to the other tests where only 10^{-5} mol/L of calcium nitrate was used.

Despite the fact that there are not a lot of variations among the results displayed in Figure 22, some of the effects that the various reagents displayed in each case can be discussed. For example, the fact that sodium silicate plus dextrin actually lowered the separation efficiency slightly than in the case where sodium silicate was used alone may indicate that the dextrin behaved as an additional dispersant in this system. However, the separation efficiency and water recovery difference between the two cases were minimal and so it is more likely that dextrin did not play much of a role at all.

The addition of starch after sodium silicate did produce a relatively good separation efficiency. Depending on the speed and time of agitation, flocs can breakup to some degree as is evident in Figure 22. A speed of 1800 rpm is an extremely high speed and so it should be of no surprise that the separation efficiency for the system consisting of sodium silicate and starch was lowered by using such intense agitation. However, despite the use of this agitation, the amount of quartz and hydroxylapatite recovered were not altered drastically. Such results are in agreement with the earlier results discussed in the last section where it was found that although flocs, whether hydrophilic or hydrophobic, would breakup to a certain degree using agitation, the degree of floc breakdown would not be catastrophic.

The role of a dispersant in this flotation system appears to have been minimal when considering the results discussed in this section thus far. Calcium nitrate was used for some tests to examine the effects of coagulants such as Ca^{2+} in improving the depressing effect of starch on gangue minerals. It is worth noting that regardless of the order in which sodium silicate or calcium nitrate was added during sample conditioning, flotation results did not vary much as can be seen from Figure 22. The reason why tests were performed using both arrangements was that initially it was unknown whether or not sodium silicate would hinder the effectiveness of calcium nitrate. It is also interesting to note that increasing the concentration of the calcium nitrate (from 10^{-5} to 10^{-4} mol/L) appeared to have a more negative impact on the results as observed earlier since the amount of hydroxylapatite entrained had increased somewhat. Perhaps such a result occurred due to the presence of excess calcium ions. The excess cations may have not only neutralized the charge of the hydroxylapatite particles to allow their adhesion to one another, but may have also caused complete charge reversal which would have kept the particles from joining together to form flocs. For the most part, it cannot be denied that separation efficiencies have increased significantly in the tests where calcium nitrate at a concentration of 10^{-4} mol/L was used.

5.2.4 Hydroxylapatite/Fine Quartz Flotation

Much like with hematite, various flotation tests were carried out with an equal mixture of hydroxylapatite and fine quartz. Some preliminary tests were also carried out to determine if hydrophobic flocculation would be necessary for this system much like what was performed for the hematite/fine quartz system.

5.2.4.1 Hydrophobic Flocculation

Hydrophobic flocculation followed by flotation was performed on an equal amount of hydroxylapatite and quartz at various agitation speeds (0, 100, 300, 600 and 1000 rpm) for 15 min. All tests were carried out with 50 ppm of sodium silicate dispersant, 50 ppm of corn starch depressant, and 5×10^{-4} mol/L of DDA collector. No frother was used for any of the tests. Figure 23 presents the flotation results of these various hydrophobic flocculation tests. As can be seen from this figure, the effect of agitation on breaking up the flocs is minor if any. With no agitation at all, about 34% of the hydroxylapatite and close to 80% of the quartz were recovered by flotation. When an agitation speed of 100 rpm was used, the amount of quartz recovered dropped slightly to about 75%, while the amount of hydroxylapatite recovered remained almost unchanged. From that point on the recoveries remained virtually unchanged for all the other agitation speeds examined.

Obviously from Figure 23 it can be seen that much like for the hematite/fine quartz flotation system, both the hydrophobic and hydrophilic flocs were not affected much by agitation at the various speeds. In fact it appears as if though agitation had less of an effect on the hydroxylapatite/fine quartz flotation system than it did for the hematite/fine quartz system.

5.2.4.2 Flotation Behavior of Hydroxylapatite/Fine Quartz

Figure 24 illustrates two different flotation tests, each carried out with and without agitation (i.e., hydrophobic flocculation). The separation efficiencies of the tests presented in Figure 24 are summarized below in Table 7.

Table 7: Separation Efficiencies of Cationic Collector Flotation of Fine Quartz-Hydroxylapatite Mixtures at pH 10 with Various Reagents

Reagent	Water Recovery, %	S.E, %
Na silicate + starch+ DDA	13.8	44.2
Na silicate dextrin + DDA	13.2	32.6
Na silicate + starch +DDA + agitation (600 rpm, 15 min)	16.4	39.2
Na silicate + dextrin + DDA + agitation (600 rpm, 15 min)	19.9	26.6

When agitation was used, it was carried out at 600 rpm for 15 min. In the absence of agitation it can be seen that about 34% of hydroxylapatite and 78.4% of quartz were recovered when sodium silicate and starch were used together. However, with agitation and at a slightly higher water recovery, the mineral recovery results remained almost unchanged with only slightly less quartz and slightly more hydroxylapatite being recovered for the same reagents. When sodium silicate and dextrin were used together, only about 58% of quartz and 25% of the hydroxylapatite were recovered. However, with agitation, the amount of quartz and hydroxylapatite recovered increased but to a much lesser degree for quartz than for hydroxylapatite. In general, it appears by looking at the results of Figure 24 that dextrin was more efficient in minimizing the entrainment of hydroxylapatite than corn starch regardless of whether or not agitation was used.

5.2.4.3 Hydroxylapatite and Fine Quartz Flotation Behavior as a Function of pH

Since starch is a known and well used depressant in many mineral flotation systems, the question arises as to why it performed poorly in the hydroxylapatite/fine quartz flotation system. One of the ways this can be investigated is by performing a number of flotation tests at various pH values and examine what effect each pH has on the recovery of each mineral in this system. These tests were in fact conducted first on each individual mineral alone, and then on an equal mixture of both hydroxylapatite and quartz. Figures 25 through 28 illustrate the effect of pH on the amount of minerals recovered. The concentration of the reagents used was 100 ppm.

Figure 25 illustrates the recovery of quartz as a function of pH. The concentration of the DDA collector used in these tests was only 10^{-5} mol/L which was less than that used in the actual two mineral flotation tests of quartz and hydroxylapatite. For the most part the results indicate that regardless of pH, the recovery of quartz was low and dependent on water recovery to some degree. It should also be noted that water recovery itself was found to be dependent on pH. For example at pH 8 the froth was observed to be extremely powerful, causing a lot of the froth to overflow from the cell at a rapid rate. On the other hand, at pH 12, the froth was observed to be extremely weak leading to difficulties in properly recovering any minerals.

Figure 26 presents the recovery of quartz as a function of pH at a higher DDA concentration (10^{-4} mol/L). This DDA concentration was the concentration used for all flotation tests in this thesis. Much like the results displayed in Figure 25, the highest amount of quartz recovered occurred at pH 8, while the lowest recovery occurred at pH 12. These recovery behaviors were a direct result of the froth characteristics at these pH values. The higher amount of quartz recovered in these set of tests was obviously due to the higher DDA concentration used. This higher DDA concentration allowed for better flocculation of quartz. Although the amount of quartz recovered was significant at pH 8, the amount of hydroxylapatite entrained also increased. For this reason tests could not be conducted at pH 8.

The effect of pH on the recovery of hydroxylapatite is illustrated in Figure 27. Much like the results for quartz, the recovery of hydroxylapatite was also observed to be significant at pH 8 indicating severe entrainment. This severe entrainment should be of no surprise considering that it was already established that the formed froth was powerful at this pH. At pH 10, 10.5, 11 and 12, the hydroxylapatite recoveries were all low. The equally low water recoveries at these pH values may have also played a role in this behavior.

In order to obtain a full picture of the effects of pH on the recovery of quartz and hydroxylapatite, it would be important to perform actual mineral flotation tests on these minerals so that more realistic and simplified results could be presented. Figure 28 presents these results. The behavior illustrated by the two curves in Figure 28 is very similar to the behavior exhibited by either mineral alone. In this figure, separation efficiency is seen as the distance between a point on the curve representing quartz recovery, at a specific pH, to the corresponding point on the hydroxylaptite recovery curve at that same pH (i.e., the greater the distance, the greater the separation efficiency). As expected the greatest separation efficiencies were produced at pH values of 10 and 10.5. The separation efficiencies at pH 8 and 12 were low which is in agreement with the results seen in the earlier figures where individually, a large amount of quartz or hydroxylapatite was recovered at pH 8, and a low amount of quartz or hydroxylapatite was recovered at pH 12.

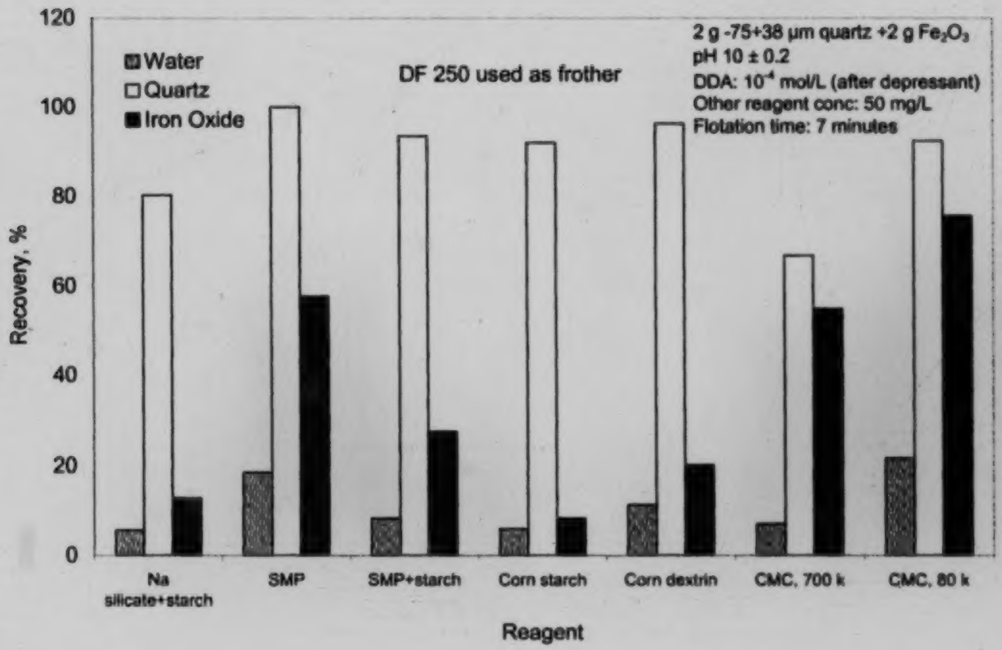


Figure 12: Hematite/Coarse Quartz Flotation Behavior

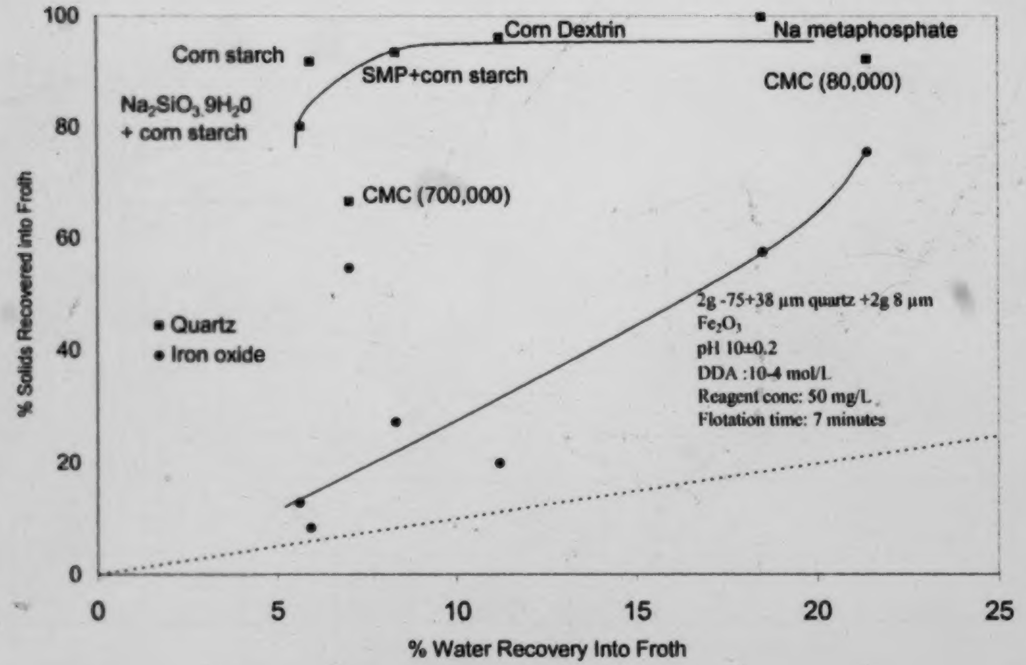


Figure 13: Alternative Representation for Hematite/Coarse Quartz Flotation Behavior

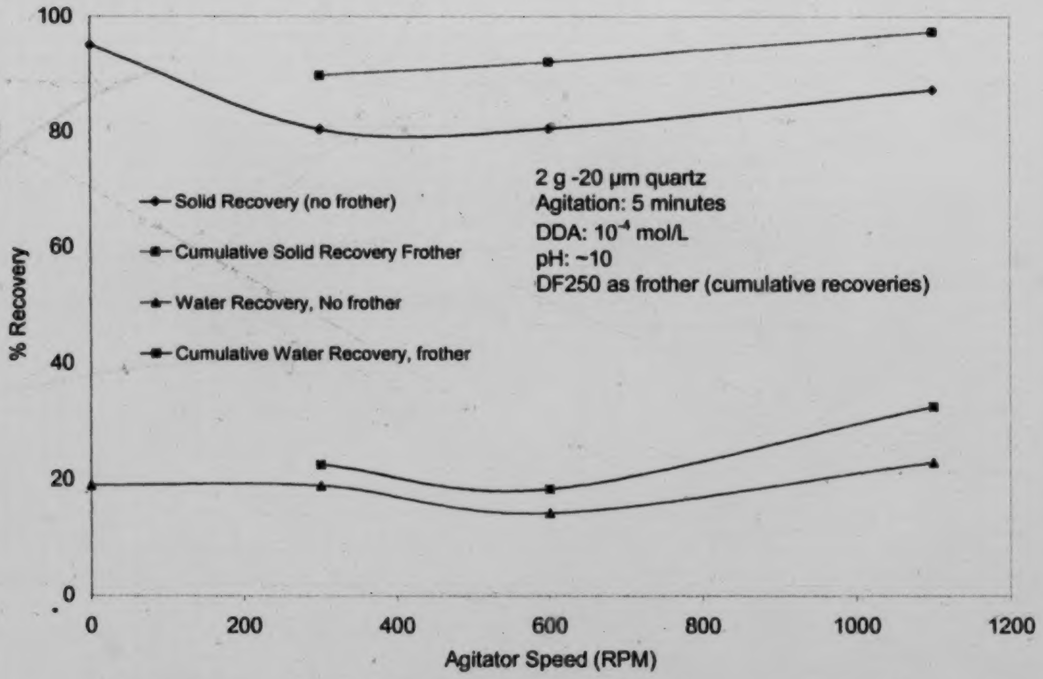


Figure 14: Quartz Recovery as a Function of Agitation Speed at 5 Minutes

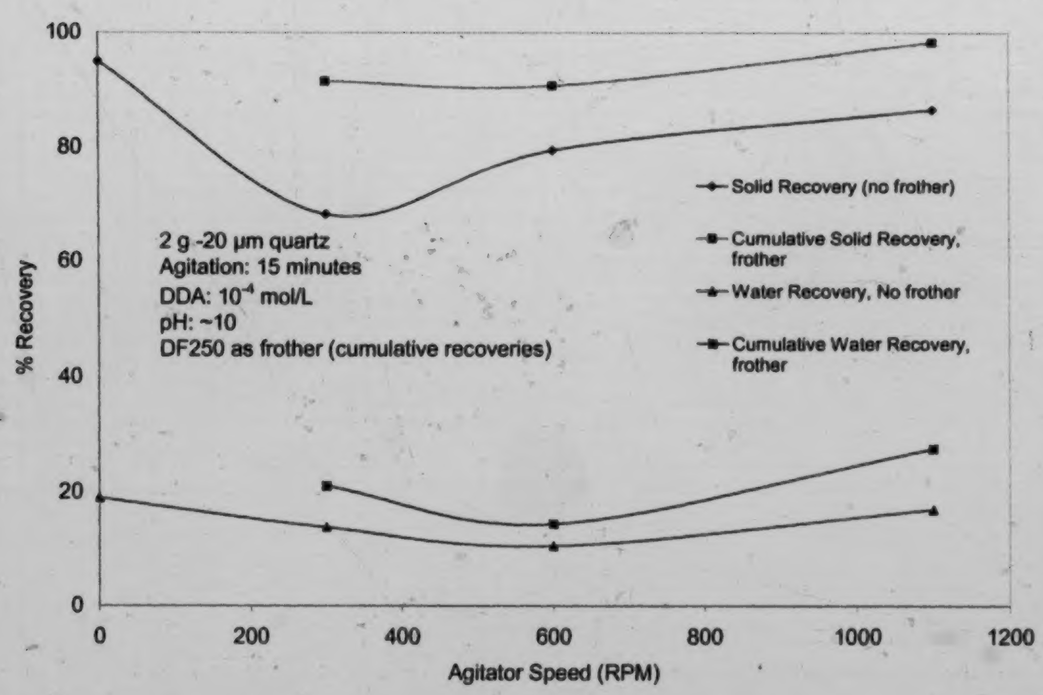


Figure 15: Quartz Recovery as a Function of Agitation Speed at 15 Minutes

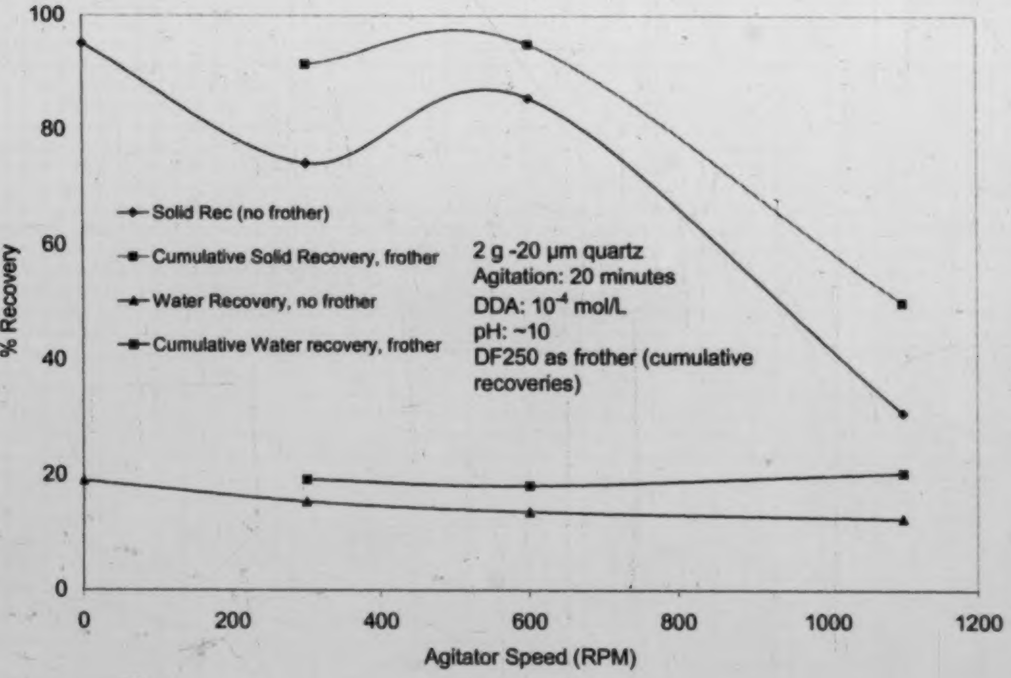


Figure 16: Quartz Recovery as a Function of Agitation Speed at 20 minutes

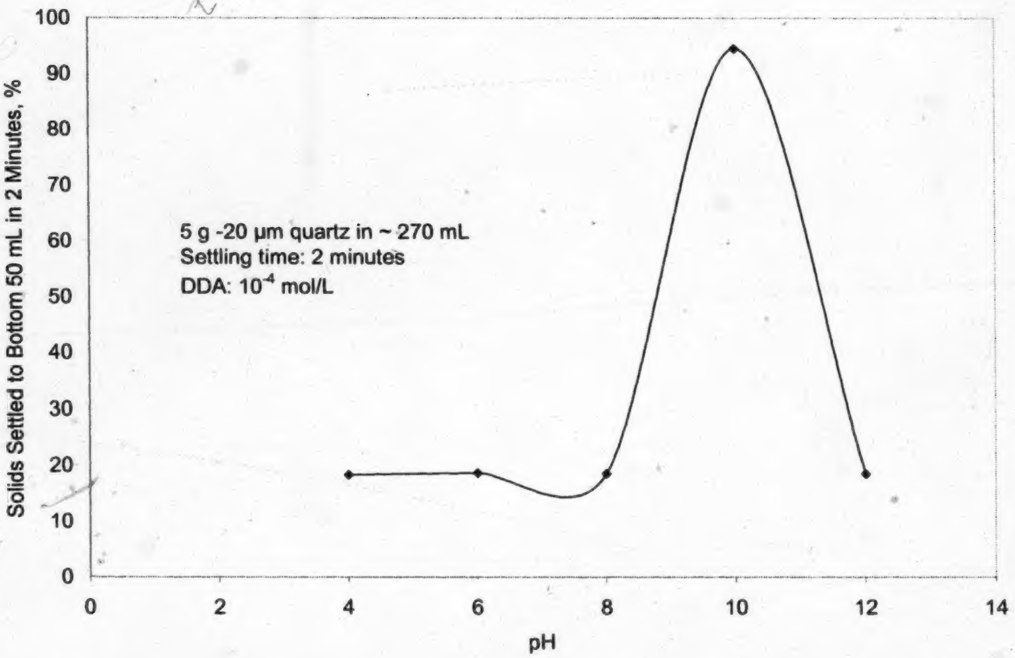


Figure 17: Influence of DDA Collector on the Flocculation of Quartz

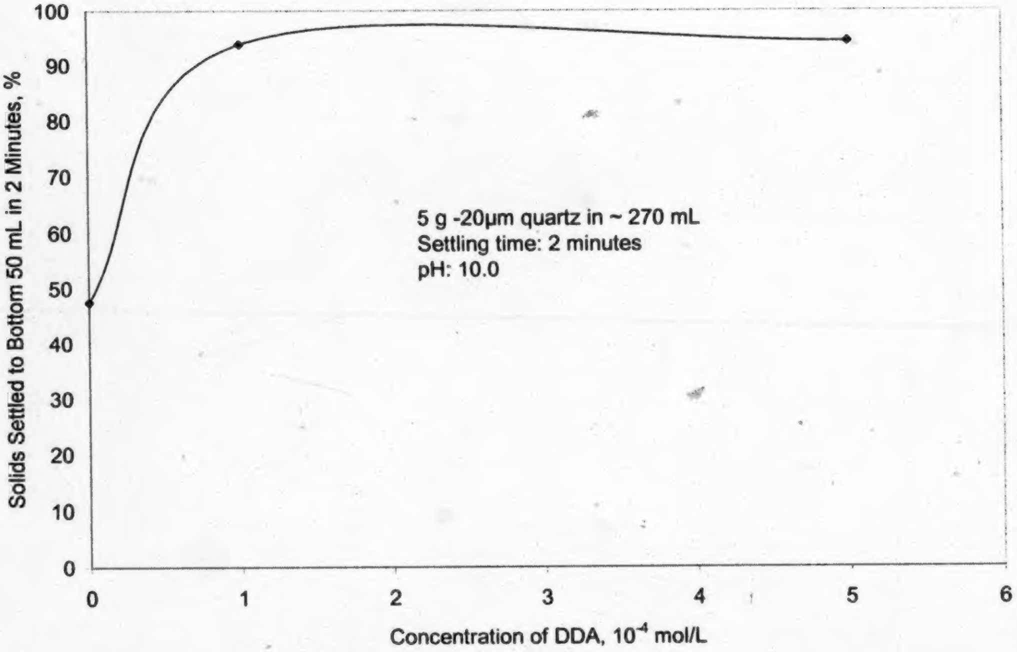


Figure 18: Quartz Flocculation Behavior as a Function of DDA Collector Concentration

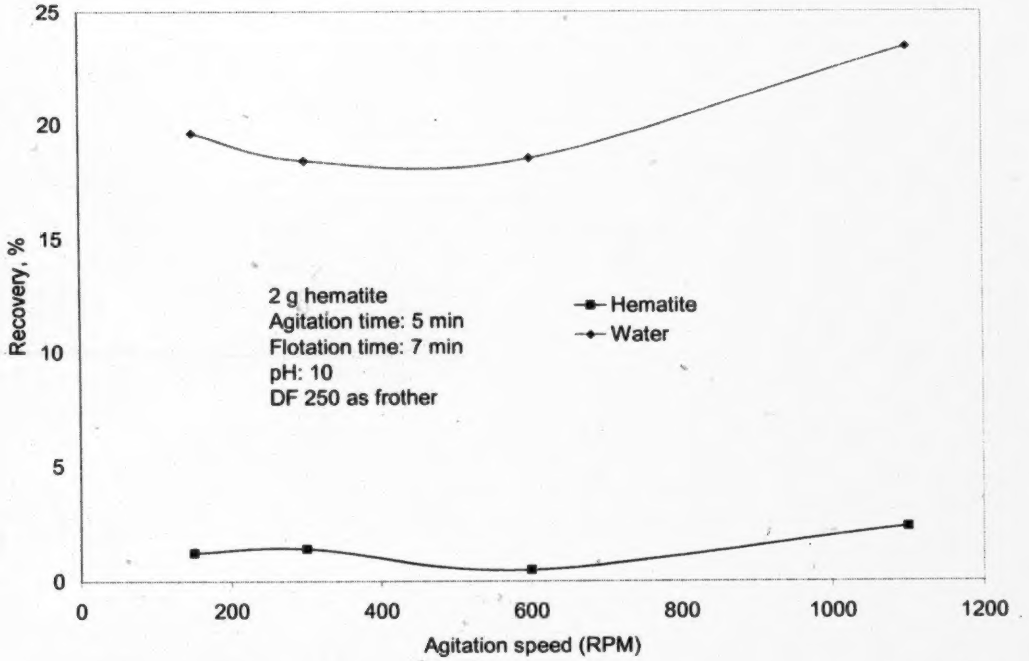


Figure 19: Hematite Recovery as a Function of Agitation Speed at 5 Minutes

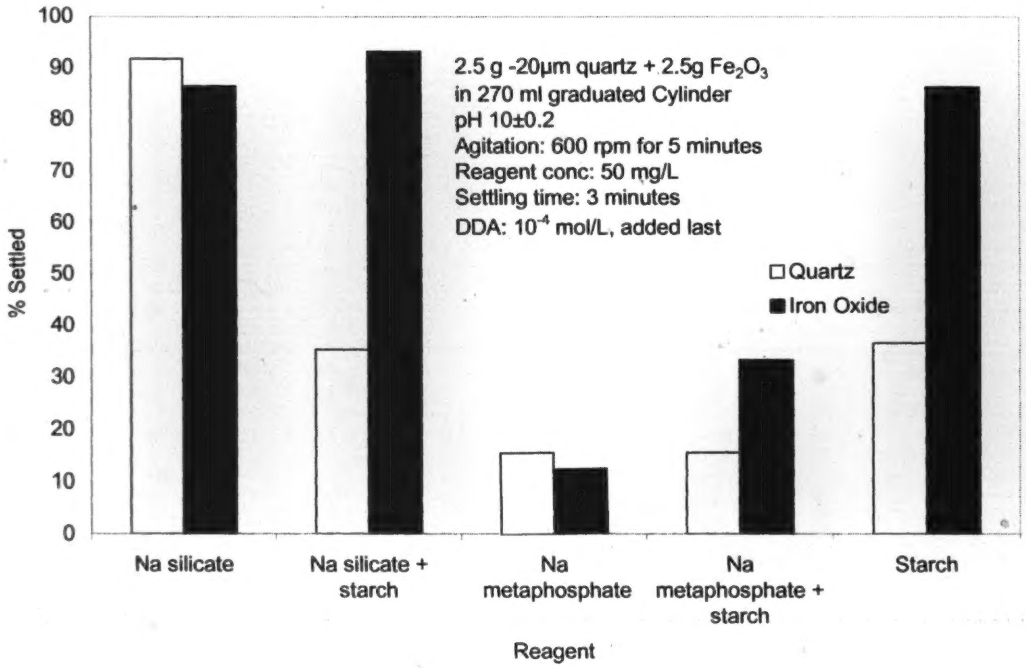


Figure 20: Hematite/Fine Quartz Flocculation Behavior

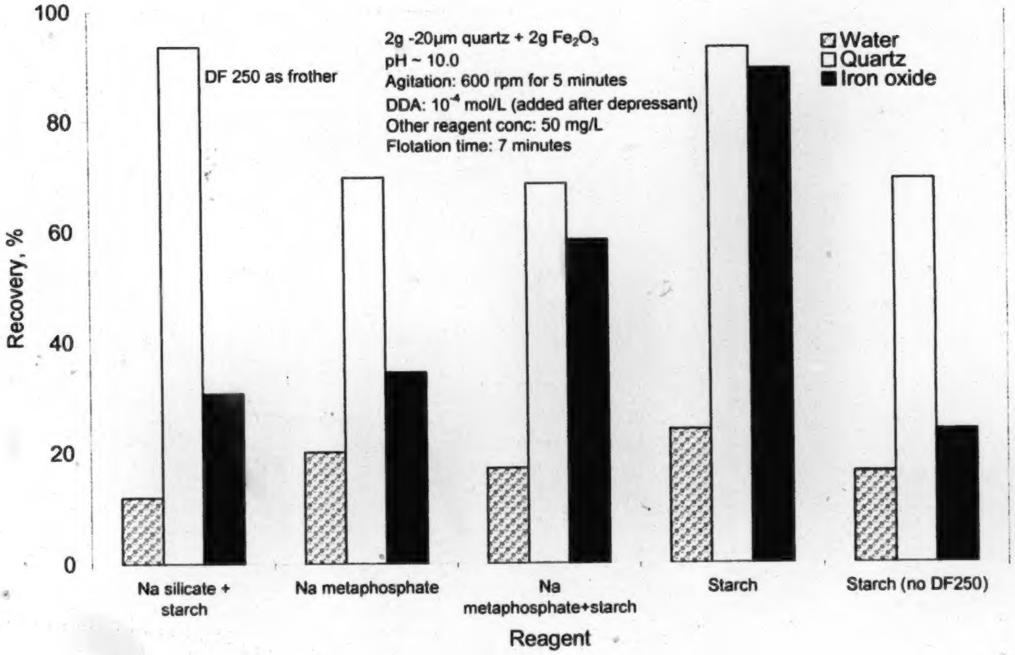


Figure 21: Hematite/Fine Quartz Flotation Behavior

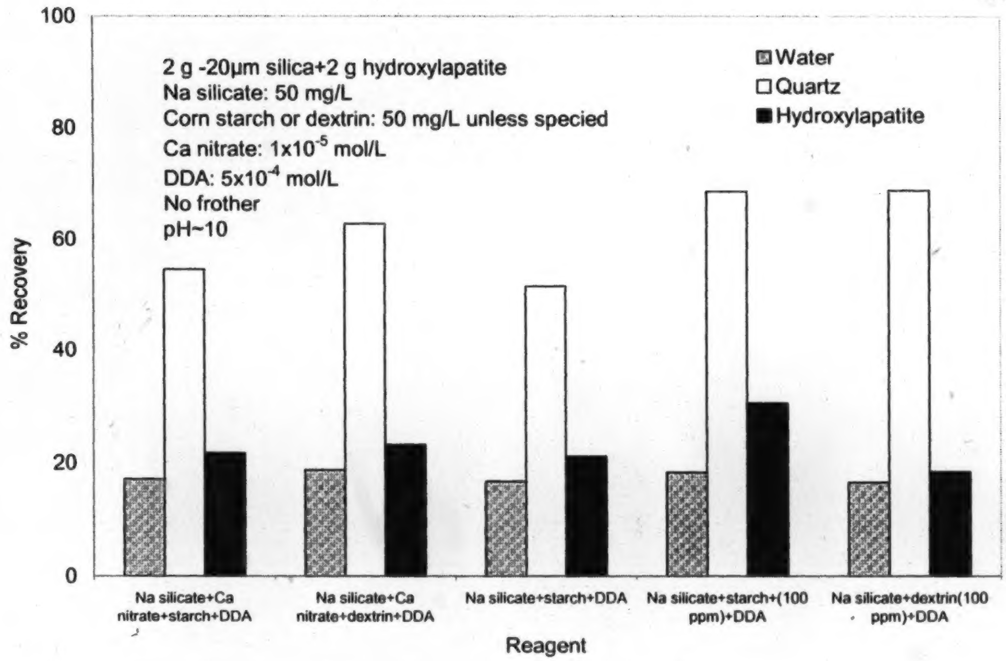


Figure 22: Hydroxylapatite/Coarse Quartz Flotation Behavior

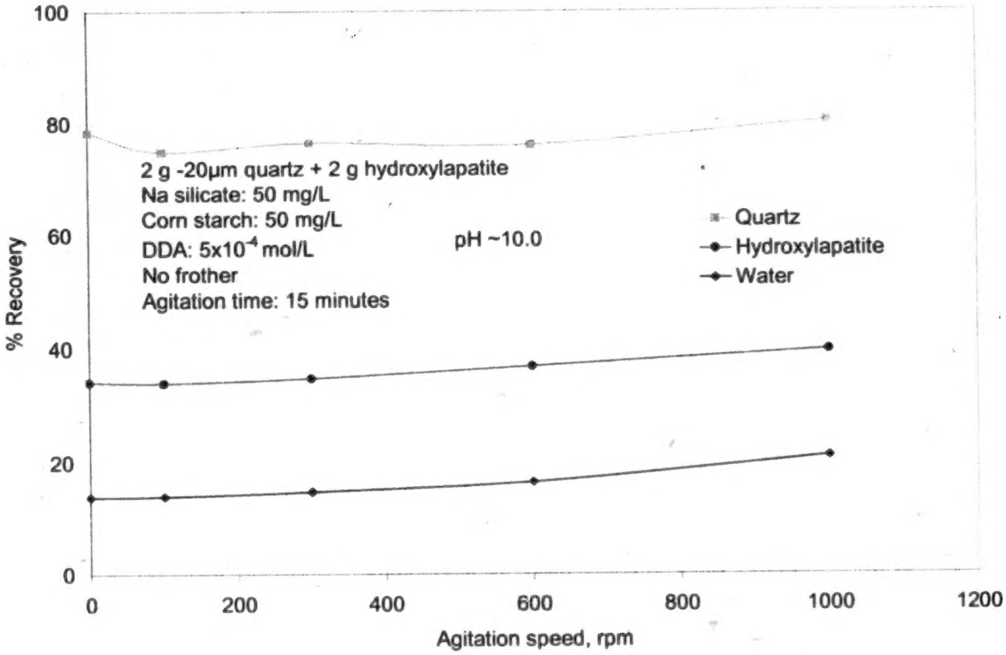


Figure 23: Hydroxylapatite/Fine Quartz Recovery as a Function of Agitation Speed at 15 Minutes

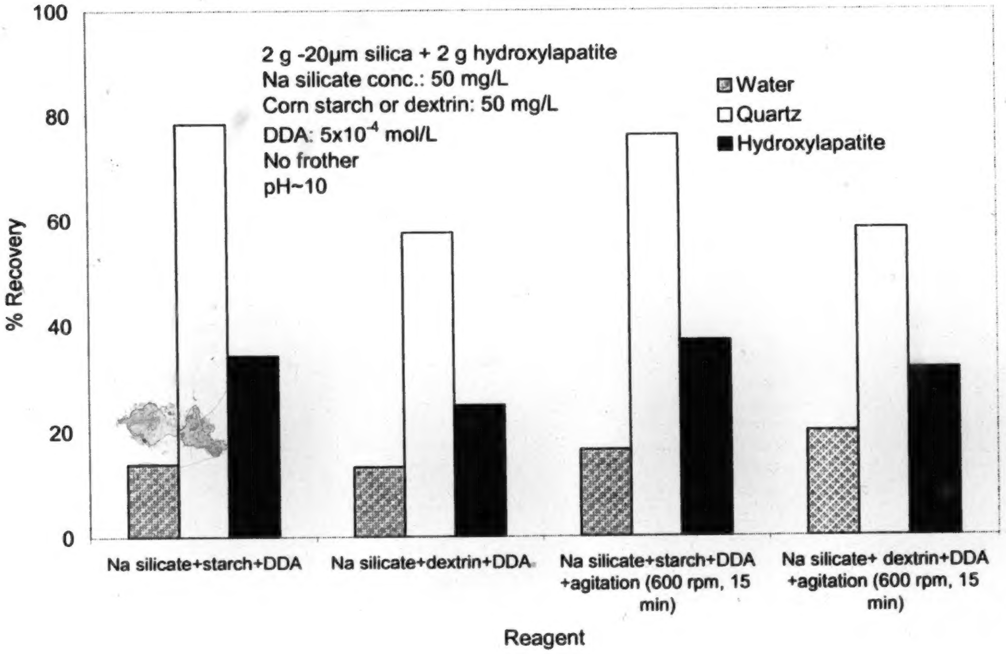


Figure 24: Hydroxylapatite/Fine Quartz Flotation Behavior

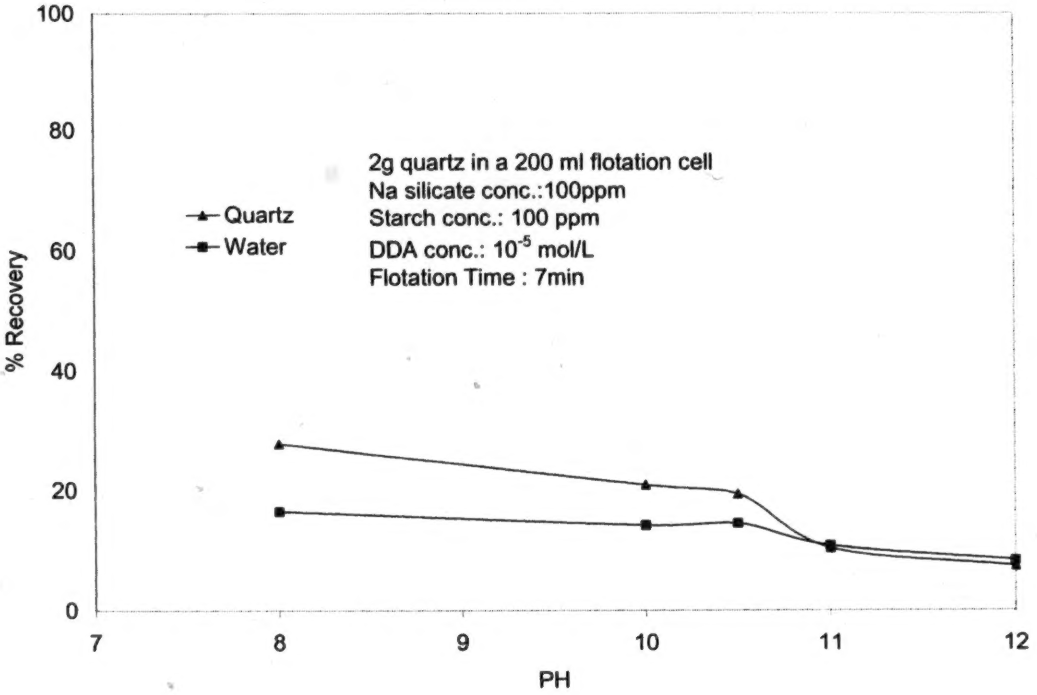


Figure 25: Quartz Recovery as a Function of pH at a DDA Concentration of 10^{-5} mol/L

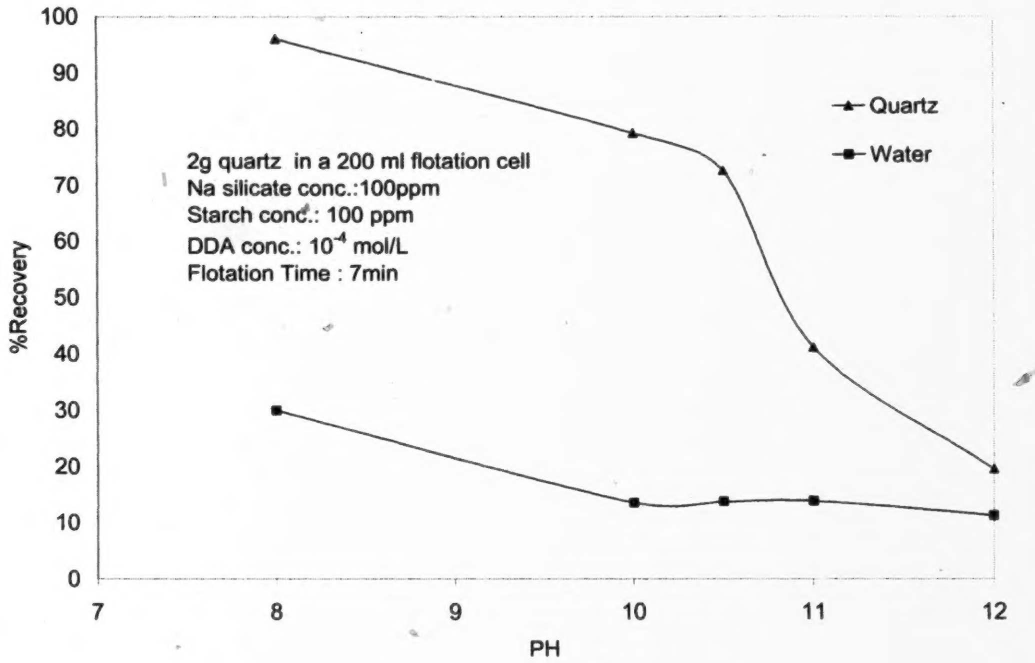


Figure 26: Quartz Recovery as a Function of pH at a DDA Concentration of 10^{-4} mol/L

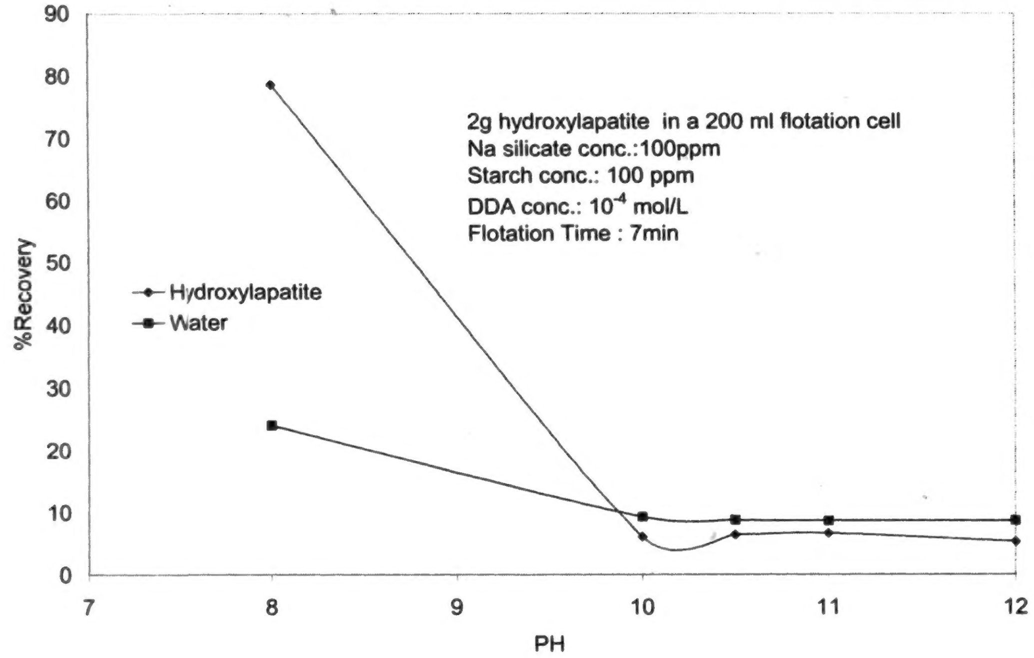


Figure 27: Hydroxylapatite Recovery as a Function of pH at a DDA Concentration of 10^{-4} mol/L

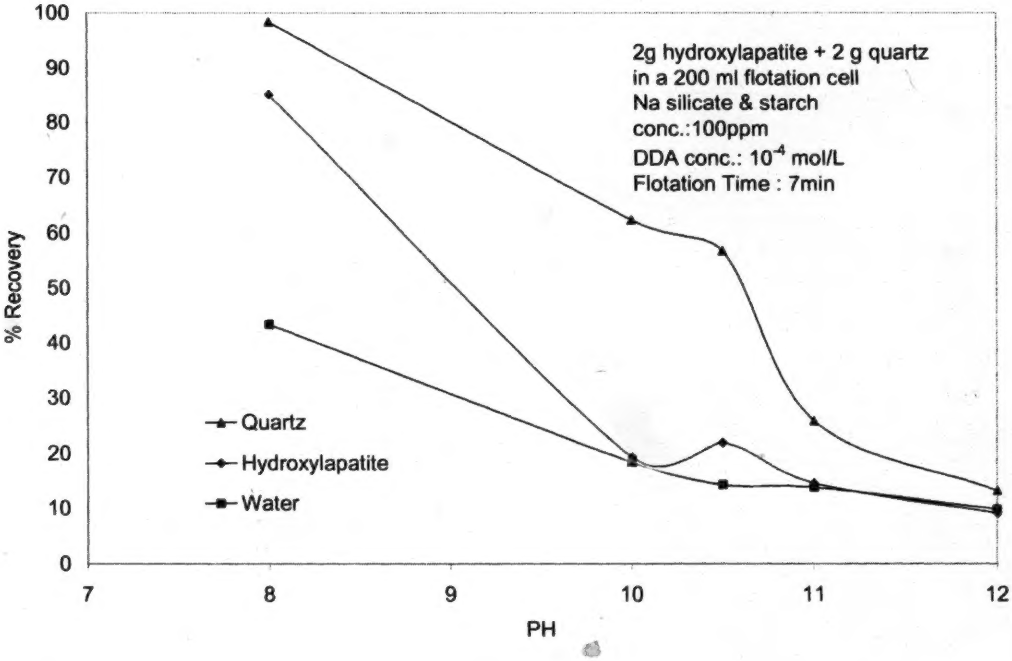


Figure 28: Hydroxylapatite/Quartz Recovery as a Function of pH at a DDA Concentration of 10^{-4} mol/L

5.3 Mechanistic Aspect of the Reduction of Entrainment

5.3.1 Particle Size Analysis

Throughout all of the tests discussed in this research, it has been observed that minerals responded differently to different reagents. These various behaviors were also observed to be affected by pH. Since one of the objectives of this thesis was to verify the positive correlation between the mechanical entrainment of hydrophilic particles and particle size, it was important to carry out tests to examine how various reagents influence particle size. Results from such analysis could in turn be used to explain the increase or decrease in entrainment of particles under the influence of various reagents and conditions. For this reason particle size analysis tests were conducted. Unfortunately, due to problems encountered in using the Mastersizer 2000 particle size analyzer with fine quartz, this mineral had to be excluded from this portion of the research. As a result only hematite and hydroxylapatite were examined.

Table 8 illustrates the particle size measurements for hematite. With no reagents being used it can be seen that the median or the 50% passing size (d_{50}) for hematite was found to be 2.5 μm. Using corn starch, however, allowed the median size of the hematite particles to increase to 7.9 μm. This increase in particle size was slightly higher at pH 10 than at pH 7. However, the increase was not significant enough so as to draw any conclusions that using corn starch at pH 10 is a better choice. Sodium metaphosphate did not appear to influence the hematite particle size. Such an observation should come as no surprise considering that severe entrainment was observed for hematite using this dispersant.

Table 8: Effect of Various Reagents and Conditions on the Particle Size of Hematite

Reagent	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
None	1.3	2.5	4.9
Starch (pH~7)	4.4	7.9	13.9
Starch (pH~10)	4.7	8.3	14.3
Sodium metaphosphate (pH~7)	1.4	2.7	5.3
Sodium metaphosphate (pH~10)	1.3	2.6	6.1

Overall, it was expected that by using corn starch, the hematite particle sizes would have increased much more than that displayed by Table 8. Since entrainment is a problem for fine particles below about 10 μm, and since earlier results did indicate that the use of corn starch eliminated entrainment, the actual particle sizes of hematite may be larger than 10 μm during flotation. One argument that can be made to explain these particle size analysis results is that perhaps the use of the ultrasonic bath prior to performing size analysis allowed for a strong dispersion of particles, a procedure that was not performed prior to conducting flotation tests. In fact referring back to Figure 6, not only did the test involving the effect of starch on hematite involve no ultrasonic breaking of the particles prior to the addition of the starch during conditioning, but in addition to this no dispersant was used either. Nevertheless, even in the presence of a dispersant, the use of corn starch did perform well in depressing iron oxide during flotation, especially in comparison to other reagents. In addition to this argument, an important verification obtained from conducting particle size analysis was that starch was responsible for forming flocs of hematite. Such a verification played a crucial role for the objectives of this research.

Table 9 presents the effect of various reagents and conditions on the particle size of hydroxylapatite. As can be seen from this table, in the absence of any reagents, the 50% passing size of the hydroxylapatite was found to be about 6.4 μm. It is interesting to note, however, that with corn starch, the 50% passing size of the hydroxylapatite actually decreased. Therefore, it appears as though corn starch failed to effectively flocculate hydroxylapatite. This finding in turn may provide the answer to the question as to why corn starch failed to effectively reduce the entrainment of hydroxylapatite, especially to the levels that were encountered with hematite.

The use of sodium metaphosphate, however, provides an additional insight into the results of Table 9 since the particle sizes of the hydroxylapatite were smaller with sodium metaphosphate than with no reagents. Perhaps when no reagents were used some of the particles managed to flocculate together during conditioning, thus accounting for the larger sized particles observed for that test. If this theory were indeed the case, then this may indicate that the starch did indeed flocculate the hydroxylapatite to some degree and that the actual size of the hydroxylapatite minerals in the absence of any reagent would have been similar to that obtained with the sodium metaphosphate.

Table 9: Effect of Various Reagents and Conditions on the Particle Size of Hydroxylapatite

Reagent	**D_{10} (μm)**	**d_{50} (μm)**	**d_{90} (μm)**
None	1.1	6.4	29.2
Starch (pH~8)	1.3	5.3	23.9
Starch (pH~10)	1.2	6.3	27.9
Sodium metaphosphate (pH~10)	1.0	4.1	24.6

5.3.2 Zeta Potential Analysis

Useful important information can be obtained by performing zeta potential measurements on some of the minerals used in this research. For example, how a mineral in the presence of a dispersant or depressant responds to the cationic collector DDA, depends to some degree on the charge on the mineral under those conditions. The response of the mineral to the collector can also be predicted based on the magnitude of the charge, i.e., the more negative the charge, the better it responds to the cationic collector. Finally, the magnitude of the charge on the mineral would also provide information as to whether the mineral particles would attract or repel one another. That is, the higher the magnitudes of the charge on particles, the more likely the particles are to repel one another and vice versa. Stability is a measure as to how well particles can remain dispersed and not coagulate. Therefore, particles that repel one another are considered more stable than those that attract one another to form aggregates. A general rule of thumb is that particles more positive than + 30 mV or more negative than -30 mV are normally considered stable (www.malvern.co.uk, 2005).

Figure 29 presents the zeta potential results for the hematite mineral using various reagents at various pH values. With no reagents being used at all, the hematite particles remained stable at most of the pH range values examined. The iso-electric point of hematite based on Figure 29 lies between pH 5 and 6 which is in agreement with literature values which place the zero point of charge for hematite at a pH value between 4.2-6.9 (www.gly.uga.edu/schroeder/geol6550/CM19.htmL, 2005). The results obtained from the use of sodium metaphosphate indicate that sodium metaphosphate allowed for the strong stability of the hematite particles throughout the entire pH range examined, since the zeta potential values are all more negative than -30 mV. This result is an agreement with earlier results of Figures 5 and 6 where it was seen that sodium metaphosphate caused dispersion of hematite and thus allowed for its severe entrainment during flotation. On the other hand, the addition of starch caused the hematite particles to become very unstable throughout the entire pH range examined since all the zeta potential values are less negative than -30 mV and are actually closer to zero. Starch may also cause polymer flocculation of the hematite. This result is also in agreement with the earlier results of Figures 5 and 6 where it was found that starch effectively flocculated the hematite particles and, therefore, minimized its entrainment during flotation. The use of CMC 700 K in general has caused the hematite particles to become negatively charged at pH 4-12 as the magnitudes of the zeta potentials are all more negative than -30 mV. Such a result verifies earlier suspicions regarding the effects of adding the cationic collector DDA to these negatively charged hematite particles, resulting in the increased entrainment of the hematite into the froth. This result in turn explains why CMC 700 K is not an effective depressant in the two mineral flotation systems. Recall that CMC 700 K was found to effectively flocculate hematite and minimize its entrainment into the froth when hematite was used alone in flotation (Figures 5 and 6). This discrepancy between the results of the single and two mineral flotation tests involving hematite suggest that although hematite is negatively charged by CMC 700 K over a wide pH range, hematite particles were aggregated together by means of bridging flocculation rather than coagulation. Corn starch which is also a polymeric depressant was also found to aggregate the hematite particles through bridging flocculation; however, since very little negative charge was produced on the hematite particles when using corn starch, the addition of DDA did not allow for the entrainment of the hematite particles into the froth in the two mineral flotation system.

Figure 30 illustrates the zeta potential measurements for hydroxylapatite under the influence of various reagents and pH conditions. From this figure it can be seen that by using sodium metaphosphate (SMP), hydroxylapatite remained stable over the entire pH range tested (i.e., the charge magnitudes are more negative than -30 mV). This result is expected since it was seen that with sodium metaphosphate, entrainment of hydroxylapatite was severe and that sodium metaphosphate was a very powerful dispersant. Furthermore, the result provides a generally good idea that due to the large magnitude of the negative charge on the hydroxylapatite in the presence of SMP, the hydroxylapatite particles would be attracted to the DDA collector making the results even worse. With no reagent used, the hydroxylapatite particles were unstable at pH 6 and 8, but stable at pH 10 and 12. Once again this result indicates that at pH 10 (the pH used mostly throughout the flotation tests in this research), using no reagent would cause the hydroxylapatite particles to remain highly dispersed and thus increase entrainment. One thing that should be mentioned though is that based on the findings of Figure 30, it appears as though with sodium metaphosphate the hydroxylapatite particles were more dispersed (i.e., more stable) than in the case where no reagents were used. Such a finding perhaps indicates that in terms of particle size, the argument made in the last section regarding hydroxylapatite particles reflocculating in the absence of any reagents is indeed true. Instability throughout the entire pH range examined occurred when corn starch was used. This result with the corn starch indicates that not only were the hydroxylapatite particles attracted to each other due to their negative charge magnitudes being low and within the instability range, but that also the attraction between the hydroxylapatite particles and the DDA collector was low. Also, starch is a large molecule and could bridge hydroxylapatite particles together upon adsorption, forming polymer flocs. Finally, under the influence of the DDA collector itself, it can be seen that at pH 6, 8 and 10, the hydroxylapatite particles were unstable, while at pH 12 the particles were very stable. It cannot be certain as to whether or not the DDA collector actually allowed the flocculation of hydroxylapatite at pH 10. However, it was observed that corn starch performed better in the single mineral flotation of hydroxylapatite (refer back to Figure 9) where no DDA was used, than in the two mineral flotation system where DDA was used, and seeing that the hydroxylapatite particles were still negative under the influence of starch at pH 10, an attraction between the hydroxylapatite particles under the use of corn starch and DDA may have existed even if very minor.

One common characteristic shared among all of the curves of Figure 30 is that at lower pH values, the zeta potentials are less negative, while at the higher pH values, the zeta potentials are more negative. This result may be due to the fact that when an acid such as HNO_3 is added to the solution to lower the pH, the particles tend to acquire a more positive charge possibly due to the presence of H^+ from the HNO_3 (although the NO_3^- may also adsorb on the surface), whereas when an alkali such as NaOH is added to the solution to increase the pH, the particles tend to acquire a more negative charge due to the presence of the OH^- ions (although the Na^+may also adsorb on the surface).

Figure 31 presents the zeta potential analysis for the fine quartz particles. With no reagent being used, the iso-electric point for quartz occurred at about pH 1.5. This iso-electric point is in agreement with the literature which reports the iso-electric point for quartz at pH 1.3 to 3.7 (Manser, 1975). All the curves in Figure 31 illustrate increased stability of the quartz particles with increasing pH. The exception to this, however, is the curve representing DDA at pH 10, where the quartz particles were unstable. This behavior observed with the quartz particles in the presence of the DDA collector is consistent with the quartz flocculation behavior observed earlier in Figure 17 where actual quartz flocculation and settling occurred at pH 10 with this reagent. At pH 10, starch stabilized the quartz particles. Such a behavior is a desired quality since it indicates that starch does not adsorb on the quartz particles (at least not significantly) and is, therefore, a selective reagent. If on the other hand, the quartz particles were unstable with starch at this pH, then this would have indicated that starch was not selective, and hence quartz particles would have been flocculated together with hydroxylapatite or even hematite for that matter.

Figure 32 illustrates the effect of pH on the zeta potential of starch both in the absence and presence of DDA. Preparation of the 1 g/L starch solution for this set of tests was performed using the same procedures described earlier but with no sodium hydroxide added so that the starch particles would remain insoluble. It can be seen from Figure 32 that for the most part starch possesses low negative zeta potential values. The addition of DDA to starch caused the zeta potential values of starch to increase and turn positive for the most part. Such a behavior clearly indicates that there is somewhat of an interaction between starch and DDA. This interaction in turn suggests that DDA has the potential of being consumed by starch meaning that less DDA would be available for the target mineral. An example of this behavior can be seen from Figure 20 where when corn starch was used both alone and with sodium silicate prior to the addition of DDA in the hematite/fine quartz flocculation behavior, less than 40% of the quartz particles settled.

To provide a better illustration and summary of the effects that individual reagents had on the zeta potential values of quartz and hydroxylapatite, Figures 33-36 were created to compare the effects of each individual reagent on the zeta potential values for hydroxylapatite, hematite, and fine quartz. Obviously the results of Figures 33-36 provide a better illustration of the degree of stability that quartz and hydroxylapatite experienced under the influence of each reagent at various pH values. When corn starch was used at pH 10 (Figure 33), it can be seen that quartz was much more stable than hydroxylapatite or hematite. This behavior is desired since it indicates that the starch did selectively adsorb on the surfaces of the hydroxylapatite and hematite particles as opposed to the surfaces of quartz. However, as previously mentioned in response to DDA, both hydroxylapatite and fine quartz were observed to be unstable at pH 10 (Figure 35). This effect of DDA on both these minerals can pose a problem since it indicates that flocs containing both quartz and hydroxylapatite have a tendency to form at this pH. In saying this, however, in actual flotation tests starch is added prior to the collector. As previously mentioned, the whole purpose of starch is to not only flocculate hydrophilic minerals, but to also form an envelope around these particles to thus form a protective barrier against the effects of collectors. Nevertheless the effects, of DDA on hydroxylapatite may have played some role in the poor results obtained for the fine quartz/hydroxylapatite flotation system as seen earlier. In order to verify this, however, more tests would have to be carried out.

The effects of sodium metaphosphate on all three minerals can be seen from Figure 34. As can be seen from this figure, all three minerals displayed stability over almost the entire pH range examined. Hematite displayed the most stability among the three minerals. A possible conflict between the phosphate groups of sodium metaphosphate and hydroxylapatite may explain why the hydroxylapatite particles were not as dispersed as the hematite particles.

Figure 36 displays the zeta potential behavior patterns of the three minerals in the absence of any reagent. It is interesting to note that at pH 10, both hematite and hydroxylapatite and hematite posses similar degrees of stability as their pH values are almost identical. Quartz on the other hand is more stable than hematite and hydroxylapatite over the entire pH range examined.

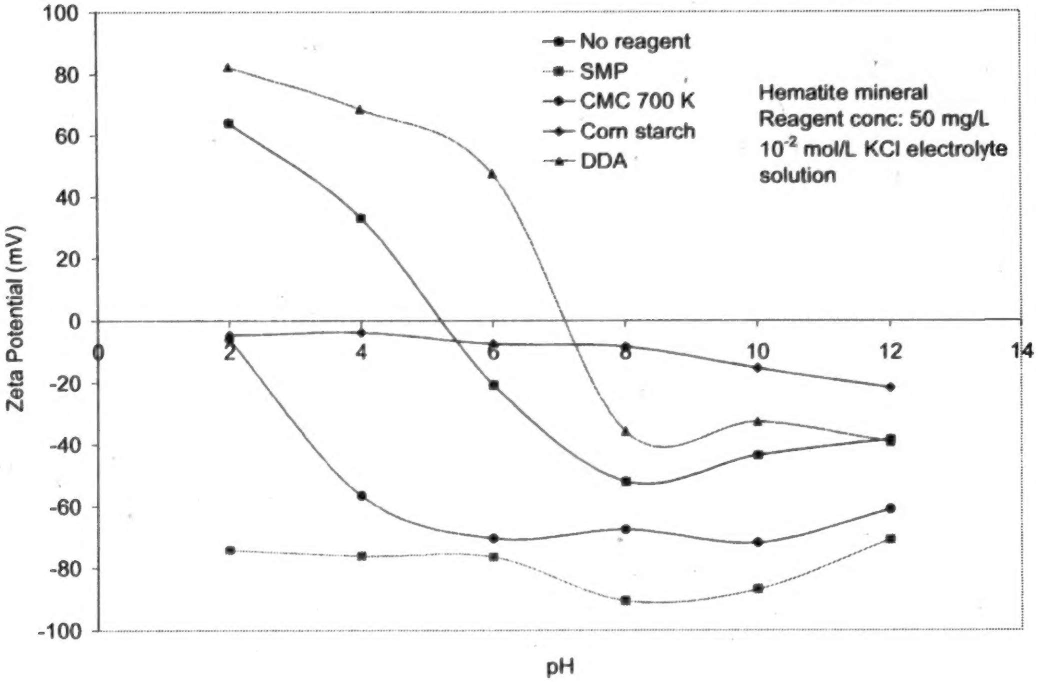


Figure 29: Effect of Various Reagents on the Zeta Potential for Hematite

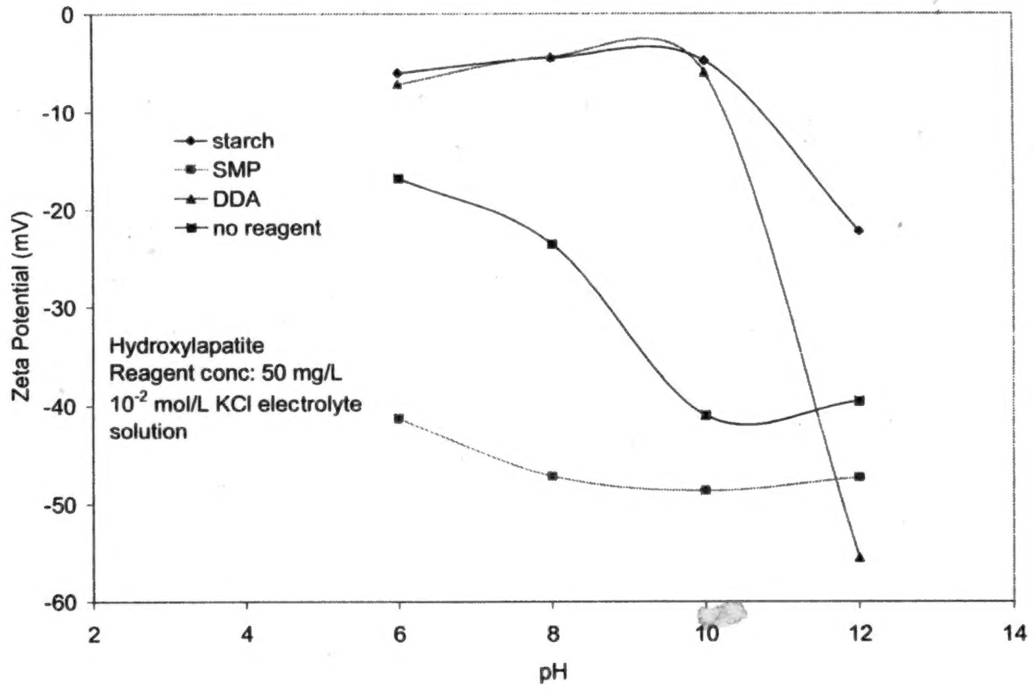


Figure 30: Effect of Various Reagents on the Zeta Potential for Hydroxylapatite

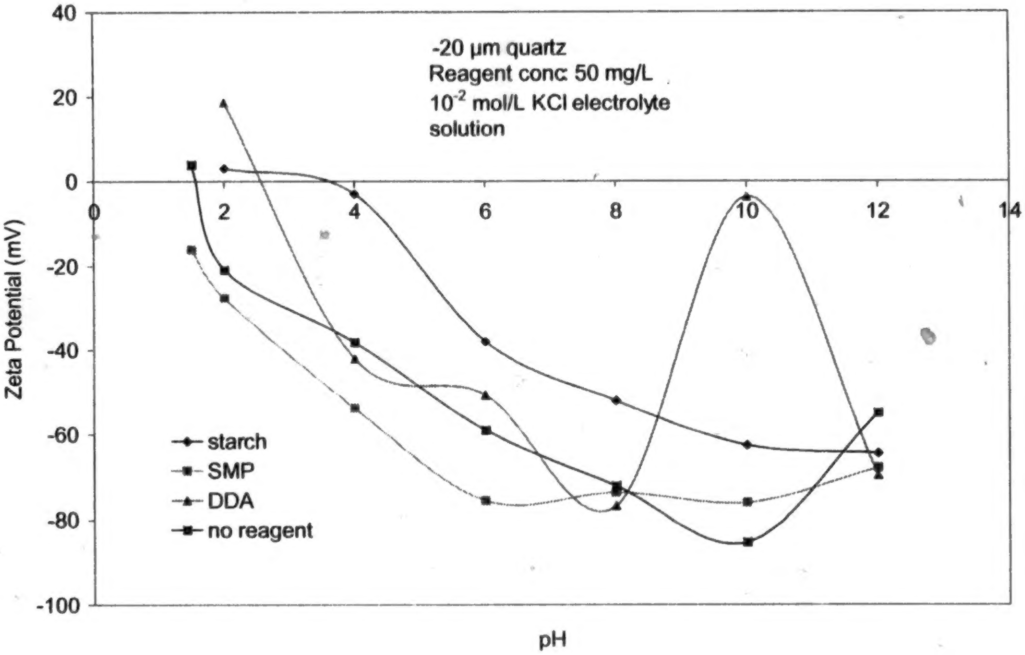


Figure 31: Effect of Various Reagents on the Zeta Potential for Fine Quartz

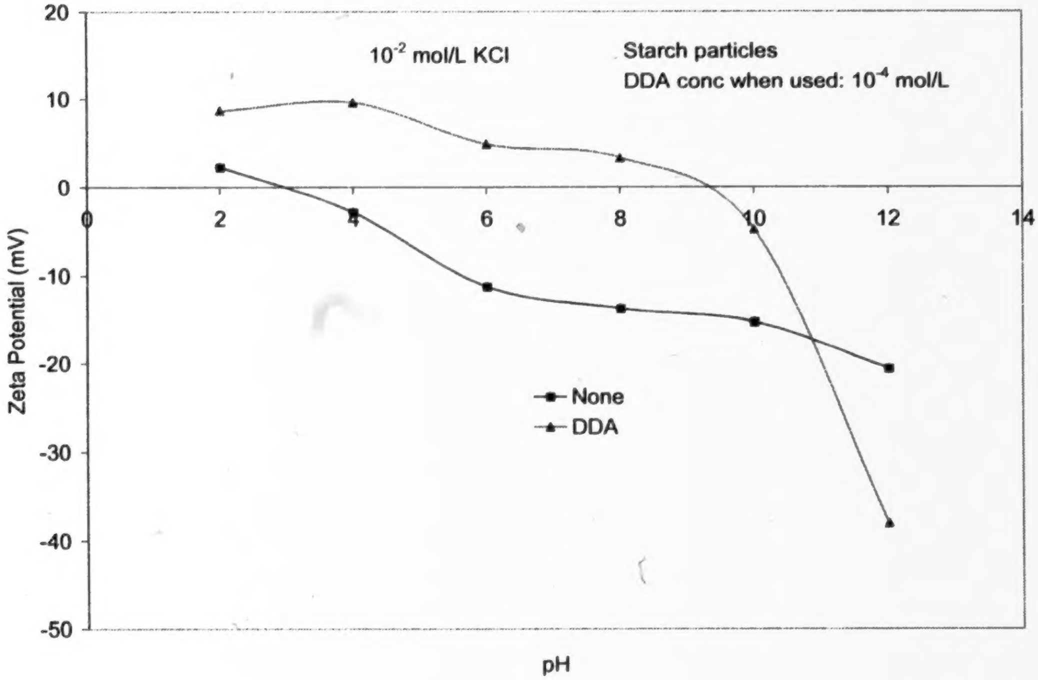


Figure 32: Effect of pH on the Zeta Potential of Starch in the Presence and Absence of DDA

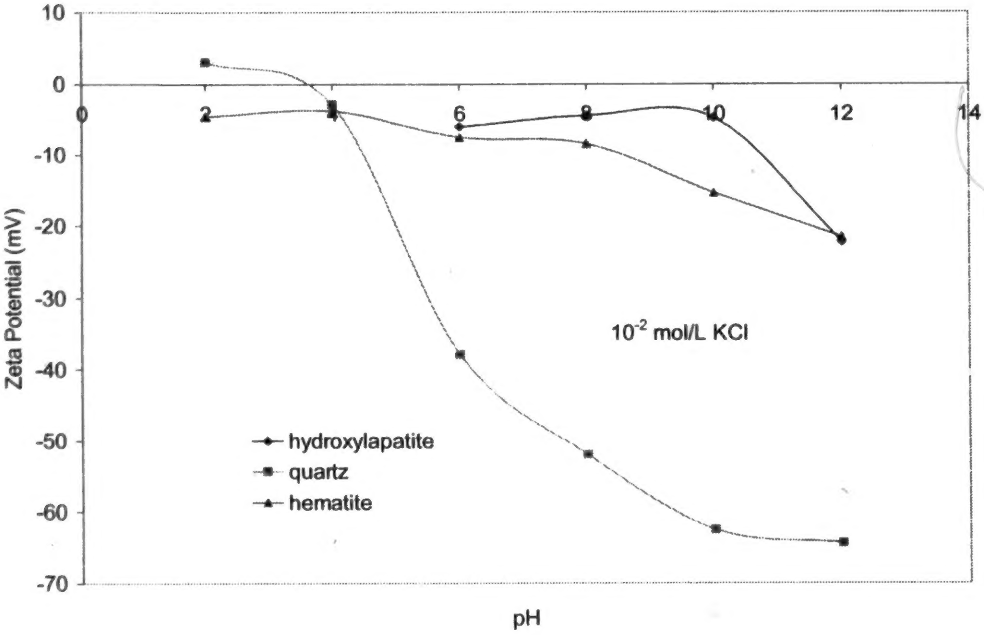


Figure 33: Effect of 50 ppm Corn Starch on the Zeta Potential for Fine Quartz, Hydroxylapatite, and Hematite

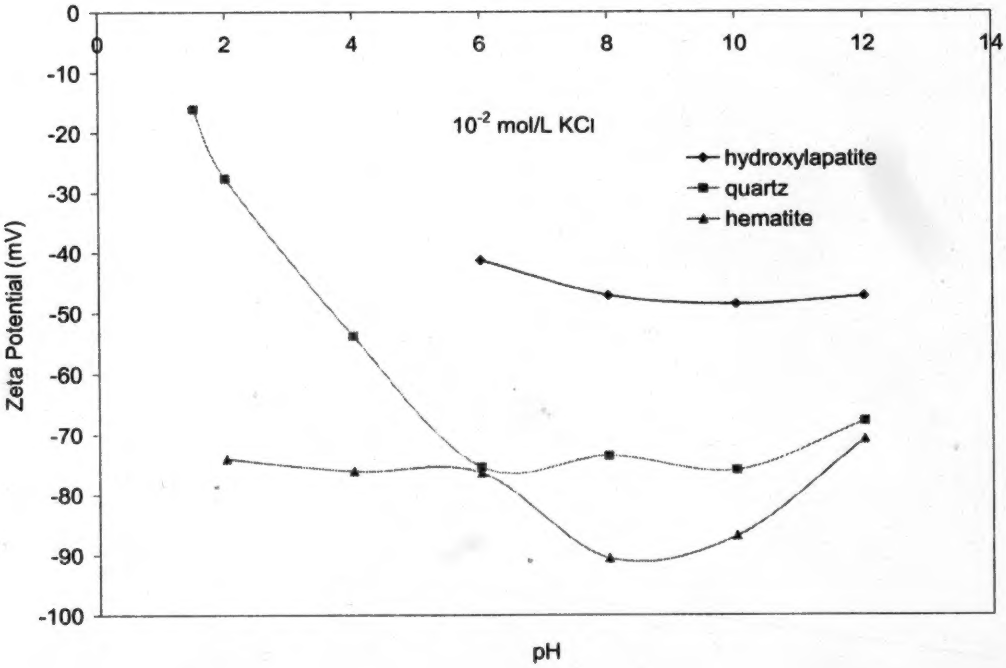


Figure 34: Effect of 50 ppm Sodium Metaphosphate on the Zeta Potential for Fine Quartz, Hydroxylapatite, and Hematite

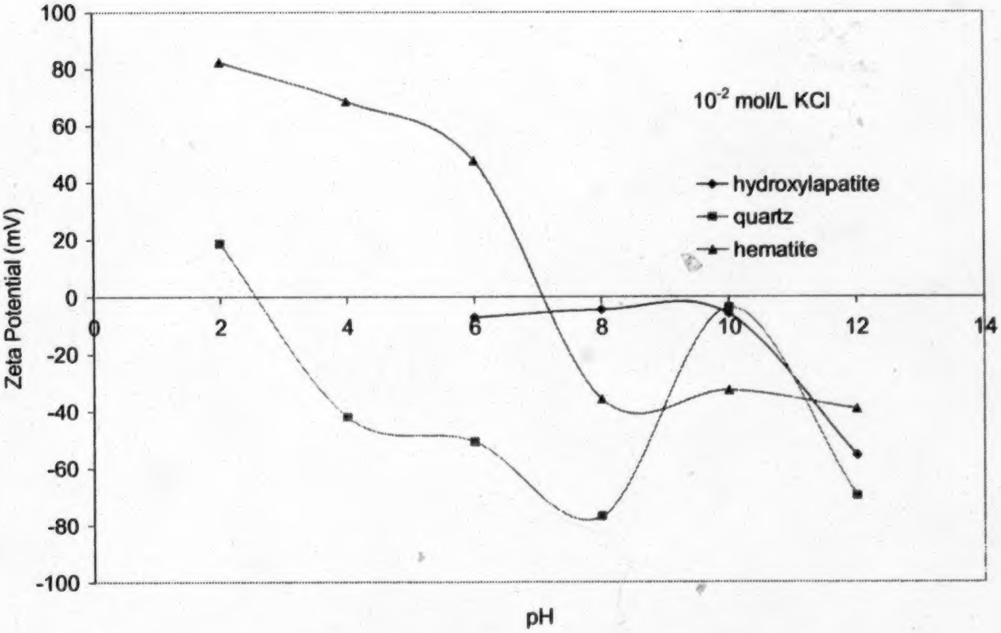


Figure 35: Effect of 10^{-4} mol/L of DDA Collector on the Zeta Potential for Fine Quartz, Hydroxylapatite, and Hematite

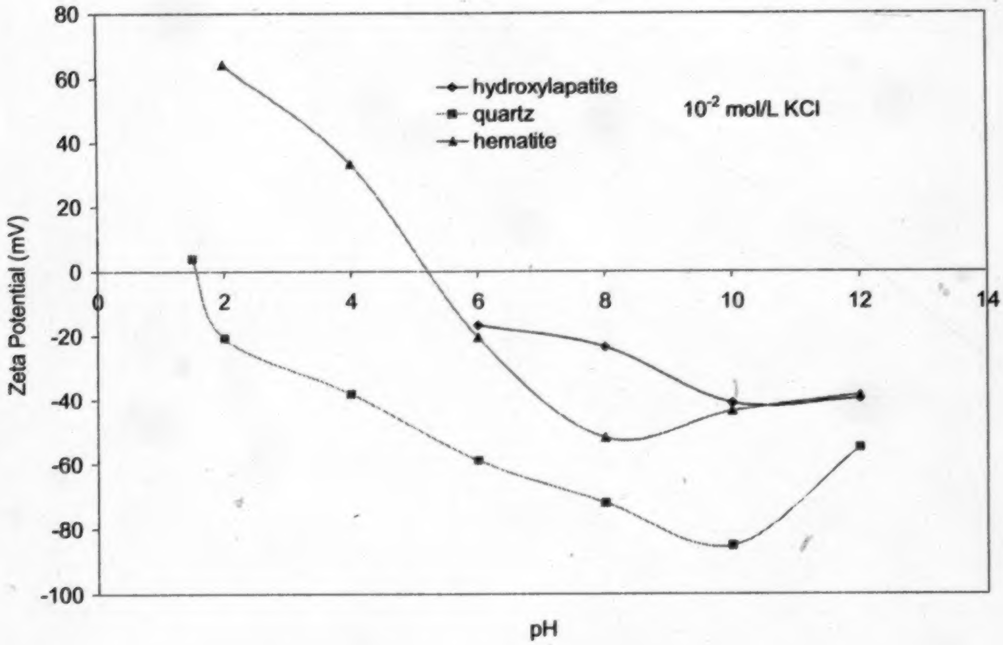


Figure 36: Effect of no Reagent on the Zeta Potential for Fine Quartz, Hydroxylapatite, and Hematite

6 CONCLUSIONS

Froth flotation is an important and commonly used mineral separation technique employed in mineral processing industries across the world. Upon receiving a ground ore, the main purpose for using froth flotation is to separate valuable minerals from gangue minerals in that ore. Once conditioned with reagents, minerals in the ore are rendered either hydrophilic or hydrophobic and are thus separated from one another by injecting gas bubbles into the flotation pulp. Unfortunately, separation of minerals through flotation is not without complications. In order to fully liberate the minerals from their ores, the ores have to be ground into very fine particle sizes. Fine particles impose two major problems in flotation. The first problem is that the fine hydrophobic particles of a mineral have a tendency to not float easily into the froth layer, resulting in a low recovery of the mineral. Many researchers have examined the reasons for the low floatability of these fine hydrophobic mineral particles and as a result, they have developed techniques and chemicals to solve this problem. The second problem is that fine hydrophilic particles may "float" into the froth product through mechanical entrainment causing lower grade of the concentrate. Entrainment is common to both hydrophilic and hydrophobic particles; however, it is hydrophilic entrainment that is a problem. Not much research has been done to minimize mechanical entrainment of fine hydrophilic particles in flotation.

The objective of this research was to verify that a high degree of entrainment is associated with fine particle sizes and to minimize that entrainment by increasing the particle sizes through exposing the minerals to a number of depressants and conditions (pH). The minerals that were rendered hydrophilic in this research included hematite (high purity iron (III) oxide, $d_{50} = 2.5$ μm) and hydroxylapatite ($d_{50} = 6.4$ μm), while quartz both coarse (-74+38 μm) and fine (-20 μm), was rendered hydrophobic. The sulphide minerals, sphalerite (-38 μm) and galena (-38 μm) were also treated as hydrophilic minerals; however, not many tests were performed with these two minerals.

The major findings of this research are:

1. Between pH 4 and 12 corn starch was found to be an effective flocculant for hematite. Carboxymethylcellulose (CMC) with a molecular weight of 700,000 was found to be an effective depressant for hematite at pH 2 to 10. Regardless of the pH used, sodium metaphosphate appeared to be a powerful dispersant for hematite causing the severe entrainment of hematite. The lower molecular weight CMC (M.W = 80,000) appeared to behave as a powerful flocculant at pH 2 and as a powerful dispersant at pH 12. In between these two pH values the lower molecular weight CMC possessed intermediate flocculation power.

2. The correlation between the degree of flocculation and mechanical entrainment was clearly observed. For the collectorless flotation of hematite, the lowest entrainment corresponded to the highest degree of flocculation, and vice versa.

3. Both corn starch and the higher molecular weight CMC were found to flocculate hydroxylapatite and minimize its entrainment at pH 10. The higher molecular weight CMC performed better than corn starch for this mineral. The lower molecular weight CMC performed much like a dispersant for hydroxylapatite with results almost identical to those of sodium silicate. Much like with hematite, sodium metaphosphate was found to be a powerful dispersant causing severe entrainment of the hydroxylapatite.

4. For the majority of reagents tested, both sphalerite and galena showed genuine flotation in the collectorless flotation tests. This behavior was most likely due to the possibility of these minerals being slightly oxidized.

5. For the hematite/coarse quartz flotation system, it was observed that at a similar water recovery, the use of corn starch depressant alone appeared to produce better separation efficiency results than when sodium silicate dispersant was added prior to the starch depressant. However, a logical explanation for this may be that

without a dispersant, the recovery of more quartz and less hematite particles may have appeared to be the case while in fact some of the hydrophilic hematite particles may have actually been attached to the hydrophobic quartz flocs through slime coating . The higher molecular weight CMC which was previously seen to be an effective depressant for hematite failed to produce similar results in this two mineral flotation system. In fact this CMC reagent yielded the worst separation efficiency result among the reagents tested for this system. It is believed that the reason as to why this higher molecular weight CMC produced such a result, was due to the possibility that this CMC placed a negative charge on the hematite particles. Therefore, when the cationic collector DDA was added, it attracted the negatively charged particles causing their entrainment into the froth.

6. Hydrophobic flocculation (shear) using agitation alone did not play much of a role in increasing the size of the hydrophobic quartz particles. Rather the hydrophobic flocs appeared to break up instead. The degree of floc degradation, however, was not significant until a speed of 1100 rpm and an agitation time of 20 min was used, where the floc breakdown was found to be significant. Agitation did not appear to break down hydrophilic flocs either. The reason for not having to use shear was that it was observed that the DDA collector was effective in forming flocs of the quartz particles at pH 10 without intensive agitation. It is for this reason that the two mineral flotation tests were carried out at this pH.

7. For the flotation test results involving hematite and fine quartz, the flotation test using sodium silicate dispersant followed by corn starch depressant produced the highest separation efficiency. Using starch alone produced the lowest separation efficiency, and the reason for this may be due to the poor selectivity resulting from the absence of a dispersant. However, a test was carried out where starch was used but in the absence of any frother and the resulting separation efficiency improved but not to the desired level. Such a result indicates that the frother promoted entrainment due to the formation of fine bubbles that it produced. This result may also explain the overall poor results observed for the hematite/fine

quartz flotation system where more than 20% of hematite was recovered in all cases.

8. For the hydroxylapatite/coarse quartz flotation system it was found that even with no reagents used, the separation efficiency was still fairly good. However, the use of the sodium silicate dispersant and corn starch depressant improved the separation efficiency to some degree by increasing the recovery of the quartz and decreasing the recovery of the hydroxylapatite. The use of calcium nitrate did improve the depression of the hydroxylapatite but not to the degree that was expected.

9. For the hydroxylapatite/fine quartz flotation system it was found that with sodium silicate used as the dispersant, corn starch did not perform as well as dextrin in depressing the hydroxylapatite particles. In addition to this it was found that the calcium ions assisted in further improving the depression of hydroxylapatite.

10. Particle size analysis tests for hematite revealed that although in the presence of starch, the hematite particle sizes have not increased above the critical size (i.e., 10 µm) (which was unexpected considering that it was found that the use of corn starch minimized the entrainment of hematite to almost negligible values), using the corn starch did increase the size of the hematite particles. According to the particle size analysis tests performed for hydroxylapatite, with no reagents being used, it appeared as though the particle size of hydroxylapatite was larger than when no dispersants or depressants were used. However it may well be that somehow with no reagents being used the hydroxylapatite particles flocculated to some degree during conditioning where stirring was used.

11. In terms of the zeta potential for hematite, hydroxylapatite and quartz, it was found that at pH 10, corn starch caused both the hematite and hydroxylapatite particles to retain a negative charge low in magnitude. Quartz, however, was found to be very stable (i.e., quartz retained a negative charge high in magnitude).

Such a result indicates that corn starch was effective in flocculating and causing both minerals to coagulate effectively while not adsorbing effectively on the surfaces of the quartz particles. The use of sodium metaphosphate dispersant allowed quartz, hematite and hydroxylapatite to remain well dispersed since these minerals were highly negatively charged with this dispersant. With the DDA collector, quartz retained a high negative charge at most pH values; however, at pH 10 the charge on the quartz particle was nearly zero, indicating that the quartz was unstable and thus well coagulated by the DDA at this pH. On the other hand, the hydroxylapatite particles were very unstable while the hematite particles were relatively stable at this pH. The DDA results verify that pH 10 was indeed the optimum pH for carrying out the two mineral flotation tests. Although the hydroxylapatite appeared to be unstable in the presence of DDA at this pH, the fact of the matter is corn starch is actually added prior to the DDA during flotation and so the corn starch assists in forming an envelope around the hydroxylapatite to prevent the adsorption of the collector on the hydroxylapatite particles.

7 RECOMMENDATIONS FOR FURTHER RESEARCH

As with any research conducted, often times it is observed that more tests can be carried out to verify observed results and expand on the findings of others. A number of recommendations that can be made based on the findings of this research include:

1. Performing the tests conducted in this research with actual industrial ores. By using actual ores, the results obtained through flotation of the minerals in those ores can be used to verify the results obtained in this research. This theory is especially true considering that the minerals used for flotation separation in industry are usually from the same ore and can contain a number of different minerals, not just two.

2. Conducting the flotation tests in flotation cells with similar configurations to industrial ones.

3. Performing molecular weight analysis on the various reagents used in this research to verify the positive correlation between reagent molecular weight and flocculation/depression of minerals.

4. Conducting flotation tests on other fine mineral types such as sulfides. Unfortunately, the preliminary tests performed on galena and sphalerite in this research did indicate that these minerals were slightly oxidized thus causing the genuine flotation behavior observed. By performing flotation tests on non-oxidized sulfide minerals as well as other mineral groups, it can be determined whether or not any of the successful results obtained in this research would be applicable to these various minerals.

5. Performing an in depth analysis to determine whether water recover or poor flocculation of a reagent effects the amount of hydrophilic particles entrained into the froth. Although entrainment is often proportional to water recovery, the

degree of flocculation performed by a reagent can also effect entrainment. It was beyond the scope of this thesis to actually determine which phenomenon was responsible for some of the results observed earlier, and so a detailed analysis is recommended.

8 REFERENCES

1. Ahmed, N. and Jameson, G.J., "The Effect of Bubble Size on the Rate of Flotation of Fine Particles," International Journal of Mineral Processing, Vol.14, 1985, 195-215.

2. Araujo, A.C., Viana, P.R.M. and Peres, A.E.C., "Reagents in Iron Ores Flotation," Minerals Engineering, Vol. 18, 2005, 219-224.

3. Arbiter, N. and Harris, C.C., "Flotation Kinetics," Froth Flotation, Fuerstenau, D.W., AIME, New York, 1962, 215.

4. Arol, A.I. and Iwasaki, I., "Effect of Sodium Silicate on Flocculation of Hematite with Starch in the Presence of Calcium," Separation Science and Technology, Vol. 38, No.3, 2003, 647-659.

5. Bisshop, J.P. and White, M.E., "Study of Particle Entrainment Into Flotation Froths," Transactions of the Institution of Mining and Metallurgy C. Mineral Processing and Extractive Metallurgy, Vol. 85, Dec. 1976, C191-C194.

6. Capponi, F., Matiolo, E., Nunes, D.G., Rubio, J., Guerrero, C.P. and Berkowitz G., "Advances in Flotation of Mineral Fines." Retrieved October 22, 2003, from http://www.lapes.ufrgs.br/Laboratorios/ltm/pdf/Advances%20in%20mineral%20fines%20flotation.pdf.

7. Cebeci, Y., "Investigation of Kinetics of Agglomerate Growth in Oil Agglomeration Process," Fuel, Vol.82, 2003, 1645-1651.

8. Cilek, E.C. and Yilmazer, B.Z., "Effects of Hydrodynamic Parameters on Entrainment and Flotation Performance," Minerals Engineering, Vol. 16, 2003, 745-756.

9. Collins, G.L. and Jameson, G.J., "Double-Layer Effects in the Flotation of Fine Particles," Chemical Engineering Science, Vol.32, 1977, 239-246.

10. Collins, G.L. and Jameson, G.J., "Experiments on the Flotation of Fine Particles: The Influence of Particle Size and Charge," Chemical Engineering Science, Vol.31, 1976, 985-991.

11. Denger, V.R. and Person, P.L., "Leeds Column Performance Evaluation," Minerals Engineering, Vol. 4, 1991, 935.

12. Derjaguin, B.V. and Shukakidse, N.D., "Dependence of the Floatability of Antimonite on the Value of Zeta-Potential," Progress in Surface Science, Vol. 43 No. 1-4, May-August 1993, 267-272.

13. DeVivo, D.G. and Karger, B.L., "Studies in Flotation of Colloidal Particulates Effects of Aggregation in Flotation Process," Separation Science, Vol. 5, No. 2, 1970, 145.

14. Dobby, G.S. and Finch, J.A., Column Flotation, Peragmon Press, London, 1990.

15. Falutsu, M. and Dobby, G.S., "Froth Performance in Commercial Sized Flotation Columns," Minerals Engineering, Vol. 5, No. 10-12, Oct-Dec 1992, 1207-1223.

16. Fan, A., Turro, N.J., and Somasundaran, P., "A Study of Dual Polymer Flocculation," Colloids and Surfaces A: Physiochemical and Engineering Aspects, Vol.162, 2000, 141-148.

17. Fitzpatrick, J.A. and Spielman, L.A., " Filtration of Aqueous Latex Suspensions Through Beds of Glass Spheres," Journal of Colloid and Interface Science, Vol. 43, No. 2, 1973, 350-369.

18. Guimaraes, R.C., Araujo, A.C. and Peres, A.E.C., "Reagents in Igneous Phosphate Ores Flotation," Minerals Engineering, Vol. 18, 2005, 199-204.

19. Harbort, G.J., Jackson, B.R. and Manlapig, E.V., "Recent Advances in Jameson Flotation Cell Technology," Minerals Engineering, Vol. 7, Nos. 2/3, 1994, 319-332.

20. Harris, C.C. and Khandrika S.M., "Breakage and Attrition in Laboratory Flotation Machines," Powder Technology, Vol. 45, No. 1, Nov-Dec 1985, 95-97.

21. Iwasaki, I., Carlson W.J. and Parmerter, S.M., "The use of Starches and Starch Derivatives as Depressants and Flocculants in Iron Ore Beneficiation," Society of Mining Engineers, AIME.

22. Impelllers, www.postmixing.com, 2005.

23. Iwasaki, I., Carlson, W.J. and Parmerter S.M., "The use of Starches and Starch Derivatives as Depressants and Flocculants in Iron Ore Beneficiation," Society of Mining Engineers, AIME, Vol. 244, 1969, 88-98.

24. Jordan, C.E. and Susko, F.J., "Rapid Flotation Using a Modified Bubble-Injected Hydrocyclone and a Shallow-Depth Froth Separator For Improved Flotation Kinetics," Minerals Engineering, Vol. 5, No. 10-12, Oct-Dec 1992, 1239-1257.

25. Jorge, R. (2001), "Unconventional Flocculation and Flotation Techniques." Retrieved October 22, 2003, from http://www.lapes.ufrgs.br/Laboratorios/ltm/pdf/unc.pdf.

26. Jorge, R. and Hoberg, H., "The Process of Fine Mineral Particles by Flotation With Hydrophobic Polymeric Carrier," International Journal of Mineral Processing, Vol.37, 1993, 109-122.

27. Koivistonen, P. and Kunnitinen, T., T. in Proc XVII International Mineral Processing Congress, Dresdan, 1991, 227.

28. KomLine-Sanderson, www.komLine.com, 2001

29. Laplante, A.R., Toguri, J.M. and Smith H.W., "The Effect of Air-Flow Rate On the Kinetics of Flotation 1. The Transfer of Material From the Froth Over the Cell Lip," International Journal of Mineral Processing, Vol. 11, No. 3, 1983, 203-219.

30. Leja, J., "Recent Developments in Mineral Dressing," Proc. Symp., 1953, 426-428.

31. Letmathe, C., Benker, B. and Gunther, L., "Intensification of Froth Flotation Through the Use of Ultrasound," Aufbereitungs Technik/Mineral Processing, Vol.43, No.4, 2002, 32-40.

32. Liu, Qi, "The Role of Polymeric-Depressant-Induced Flocculation in Fine Particle Flotation," 2003.

33. Malvern Instruments, www.malvern.co.uk, 2005.

34. Manser, R.M., Handbook of Silicate Flotation, 1975.

35. Miller, J.D. and Ye Y., Minerals Processing and Extractive Metallurgy Review, Vol.5, 1989, 307.

36. Miller, J.D. and Ye, Y., Miner. Process & Ext Metall Review, Vol. 5, 1989, 307.

37. Montes-Sotomayor, R., Houot, R. and Kongolo, M., "Technical Note Flotation of Silicated Gangue Iron Ores: Mechanism and Effect of Starch," Minerals Engineering, Vol. 11, No. 1, 1998, 71-76.

38. Neethling, S.J. and Cilliers, J.J., "The Entrainment of Gangue into a Flotation Froth," International Journal of Mineral Processing, Vol.64, 2002, 123-134.

39. Nicol, S.K., Engel, M.D. and Teh, K.C., "Fine-Particle Flotation In an Acoustic Field," International Journal of Mineral Processing, Vol.17, 1986, 143-150.

40. Parazak, D.P., Burkhardt, C.W., McCarthy, K.J. and Stehlin, M.P., "Hydrophobic Flocculation," Journal of Colloid and Interface Science, Vol.123, No.1, May 1988, 59-72.

41. Pavlovic, S. and Brandao, P.R.G., "Adsorption of Starch, Amylose, Amylopectin and Glucose Monomer and their Effect on the Flotation of Hematite and Quartz," Minerals Engineering, Vol.16, 2003, 1117-1122.

42. Peres, A.E.C. and Correa, M.I., "Depresion of Iron Oxides With Corn Starches," Minerals Engineering, Vol. 9, No. 12, 1996, 1227-1234.

43. Pinto, C.L.L., de Araujo, A.C. and Peres, A.E.C., "The Effect of Starch, Amylose and Amylopectin on the Depression of Oxi-Minerals," Minerals Engineering, Vol. 5, Nos. 3-5, 1992, 469-478.

44. Rajagopalan, R., Principles of Colloids and Surface Chemistry, 1997.

45. Reay, D. and Ratcliff, G.A "Experimental Testing of Hydrodynamic Collision Model of Fine Particle Collision," Canadian Journal of Chemical Engineering, Vol. 53, No. 5, 1975, 481-486.

46. Ross, V.E., "Flotation and Entrainment of Particles During Batch Flotation Tests," Minerals Engineering, Vol.3, No.3/4, 1990, 245-256.

47. Ross, V.E., "The Behavior of Particles in Flotation Froths," Minerals Engineering, Vol.4, No. 7-11, 1991, 959-974.

48. Scott, S.L. and Smith, R.W., "Diamine Flotation of Quartz," Minerals Engineering, Vol.4, No. 2, 1991, 141-150.

49. Singh, R., Rao, S.S., Maulik, S.C. and Chakravorty, N., "Fine Particles Flotation-Recent Trends," Trans. Indian Inst. Met., Vol.50, No.5, October 1997, 407-419.

50. Sis, H. and Chander, S., "Reagents used in the Flotation of Phosphate Ores: A Critical Review," Minerals Engineering, Vol. 16, 2003, 577-585.

51. Sivamohan, R. and Forssberg, E., "Recovery of Heavy Minerals from Slimes," International Journal of Mineral Processing, Vol. 15, No. 4, 1985, 297-314.

52. Smith, P.G., and Warren, L.J., "Entrainment of Particles into Flotation Froths," Mineral Processing and Extractive Metallurgy Review, Vol. 5, 1989, 123-145.

53. Song, S., Lopez-Valdivieso, A. and Ding, Y., "Effects of Nonpolar Oil on Hydrophobic Flocculation of Hematite and Rhodochrosite Fines," Powder Technology, Vol.101, 1999, 73-80.

54. Song, S., Lopez-Valdivieso, A. and Reyes-Bahena, J.L., "Hydrophobic Flocculation Applied to Fine Mineral and Coal Processing," XXIII Convencion AIMMGM'99, 1999, 1-20.

55. Song, S., Lopez-Valdivieso, A., Reyes-Bahena, J.L. and Lara-Valenzuela, C., "Floc Flotation of Galena and Sphalerite Fines," Minerals Engineering, Vol.14, No.1, 2001, 87-98.

56. Song, S.and Lu, S., "Advances in Fine Particle Processing, "International Symposium on Advances in Fine Particle Processing, Boston, Massachusetts, 1989, 241-247.

57. Subrahmanyam, T.V. and Forssberg, E., "Froth Characteristics and Grade Recovery Relationships in the Flotation of Lead-Zinc and Copper Ores," Minerals Engineering, Vol. 1, No. 1, 1988, 41-52.

58. Subrahmanyam, T.V. and Forssberg, E., "Froth Stability, Particle Entrainment and Drainage in Flotation – A Review," International Journal of Mineral Processing, Vol.23, 1988, 33-53.

59. Subrahmanyam, T.V. and Forssberg, K.S., "Fine Particles Processing: Shear Flocculation and Carrier Flotation- A Review," International Journal of Mineral Processing, Vol.30, 1990, 265-286.

60. The Geochemistry of Clay Minerals, www.gly.uga.edu/schroeder/geol6550/CM19.htmL, 2005.

61. Trahar, W.J., "A Rational Interpretation of the Role of Particle Size in Flotation," International Journal of Mineral Processing, Vol.8, 1981, 289-327.

62. Trahar, W.J., and Warren, L.J., "The Floatability of Very Fine Particles- A Review," International Journal of Mineral Processing, Vol.3, 1976, 103-131.

63. Wang, D.Z., Qu, G.Z. and Hu, W.B., "The Effect of Carrier-Promoting Aggregation of Coarse Particles in Fine Particle Flotation," CIM Bulletin, Vol. 81, June 1988, 99-99.

64. Warren, L.J., "Determination of the Contributions of True Flotation and Entrainment in Batch Flotation Tests," International Journal of Mineral Processing, Vol. 14, No.1, 1985, 33-44.

65. Warren, L.J., "Shear Flocculation," Chemtech, Vol. 11, No. 3, 1981, 180-185.

66. Warren, L.J., "Ultrafine Particles in Flotation," Principles of Mineral Flotation The Wark Symposium, M.H. Jones and J.T. Woodcock, Eds., The Australian Institute of Mining and Metallurgy, 1984, 185-214.

67. Weissenborn, P.K., "Behavior of Amylopectin and Amylose Components of Starch in the Selective Flocculation of Ultrafine Iron Ore," International Journal of Mineral Processing, Vol. 47, 1996, 197-211.

68. Weissenborn, P.K., Warren, L.J. and Dunn, J.G., "Optimization of Selective Flocculation of Ultrafine Iron Ore," International Journal of Mineral Processing, Vol.42, 1994, 191-213.

69. Weissenborn, P.K., Warren, L.J. and Dunn, J.G., "Selective Flocculation of Ultrafine Ore. 1.Mechanism of Adsorption of Starch onto Hematite," Colloids and Surfaces A: Physiochemical and Engineering Aspects, Vol.99, 1995, 11-27.

70. Welch, A.J.E., "The Relation of Crystal Lattice Discontinuities to Mineral Dressing. Recent Developments in Mineral Dressing," Proc. Symp., 1953, 387-392.

71. Wills, B.A., Mineral Processing Technology, 6th edition, Butterworth-Heinemann, Oxford, 1997.

72. Xstrata Technology-Jameson Cell Advantages. Retrieved March 2, 2004, from http://www.mimpt.com.au/jamesoncell-advantages.htmL.